

Gold Complexes with the Selenolate Ligand $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{Se}]^-$ Olga Crespo,[†] M. Concepción Gimeno,^{*†} Antonio Laguna,[†] Monika Kulcsar,[†] and Cristian Silvestru[‡]*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., E-50009 Zaragoza, Spain, and Facultatea de Chimie și Inginerie Chimică, Universitatea “Babeș-Bolyai”, 400663-Cluj-Napoca, Romania*

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The reaction of $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{Se}]\text{M}$ ($\text{M} = \text{Li}, \text{K}$) with the gold(phosphine) complexes $[\text{AuCl}(\text{PR}_3)]$ gives the mononuclear gold-selenolate species $[\text{Au}\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}(\text{PPh}_3)]$ (**1**) or $[\text{Au}\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}(\text{PPh}_2\text{py})]$ (**2**), respectively. The treatment of the $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{Se}]\text{M}$ with $[\text{Au}_2\text{Cl}_2(\mu\text{-P-P})]$ [$\text{P-P} = \text{bis}(\text{diphenylphosphino})\text{methane}$ (dppm), $\text{bis}(\text{diphenylphosphino})\text{ethane}$ (dppe), $1,1'$ - $\text{bis}(\text{diphenylphosphino})\text{ferrocene}$ (dppf)] derivatives gives complexes with stoichiometry $[\text{Au}_2\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2(\mu\text{-P-P})]$ [$\text{P-P} = \text{dppm}$ (**3**), dppe (**4**), or dppf (**5**)]. These complexes exhibit a different structural framework, that is, **4** crystallizes as a chain polymer with intermolecular aurophilic bonding, while **5** shows an intramolecular $\text{Au(I)} \cdots \text{Au(I)}$ interaction. The gold(III) derivative $\text{Bu}_4\text{N}[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}]$ (**6**) is obtained by reaction of $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{Se}]\text{K}$ and $\text{Bu}_4\text{N}[\text{AuBr}(\text{C}_6\text{F}_5)_3]$, in a 1:1 molar ratio. These species exhibit luminescence which probably arises from a mixed $^3\text{LMMCT}$ and ^3MC excited state. The emission properties in these complexes seem to be useful for structural predictions and lead to the proposal of intermolecular aggregation in the solid state and frozen solution for complexes **1**, **2**, **3**, whose crystal structures have not been elucidated.

Introduction

The gold chemistry has developed continuously in the last 20 years, and at present it is an extremely attractive field of research, not only for the fundamental interest (e.g., “aurophilicity the unprecedented affinity between gold atoms even with ‘closed-shell’ electronic configurations and equivalent electrical charges”)¹ but also for the potential applications in biochemistry and technology.² One special characteristic presented by some of the gold complexes is

the photoluminescence where the gold(I) derivatives possess intense, long-lived luminescence in the solid state with emission energies spanning the visible spectrum. In these compounds aggregation through aurophilic interactions play a key role in producing the emissive state.³

Chalcogenolate gold complexes, mainly thiolate gold derivatives, have been deeply studied because they are important in many fields of research since they are used in medicine as antiarthritic agents and also have shown anti-tumoral and anti-HIV activity, and in nanoscience they can act as stabilizers of metal nanoparticles and also as precursors for other sources of materials.^{4–6} However, only few gold complexes with selenolate ligands have been reported. These

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include mononuclear gold(I) complexes of the type $[\text{Au}(\text{SeR})(\text{PR}_3)]$,⁷ dinuclear compounds with bridging selenolate ligands as $[\text{Au}_2(\mu\text{-SeR})(\text{PPh}_3)_2]^+$ or with terminal selenolate ligands as in $[\text{Au}_2(\text{SeR})_2(\mu\text{-P-P})]$ [P-P = bis(diphenylphosphino)ethane, 1,1'-bis(diphenylphosphino)ferrocene],^{8,9} compounds with selenolate ligands bridging different metals,¹⁰ homoleptic species of the type $[\text{Au}(\text{SeR})_4]$, or $[\text{Au}(\text{SeR})_2]^-$,¹¹ and recently carbene selenolate gold complexes.¹² Other oxidation states are even more poorly represented, with only one gold(II) species, that is, $[\text{Au}_2\text{Cl}(\text{SePh})\{\mu\text{-(CH}_2)_2\text{PPh}_2\}_2]$,¹³ and the gold(I)–gold(III) species $[\text{Au}_4(\text{C}_6\text{F}_5)_6(\mu\text{-SePh})_2(\mu\text{-dppf})]$ or $[\text{Au}_3(\text{C}_6\text{F}_5)_3(\mu\text{-SePh})_2(\mu\text{-dppf})]$, recently reported by us.⁹ In addition, we have reported on the synthesis and structural characterization of various hyper-valent organochalcogen (Se, Te) compounds containing the 2-(Me_2NCH_2) C_6H_4 and 2-{X(CH₂CH₂)₂NCH₂} C_6H_4 (X = O, NMe) groups which might be useful as ligands in gold coordination chemistry because of the stabilizing effect induced by coordination of the nitrogen atom from the pendant arm either to selenium or gold centers.¹⁴

Here we report on the synthesis and characterization of the first gold complexes containing the organoselenolate $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]^-$ moiety. Mononuclear gold(I) complexes with monophosphine ligands, dinuclear species with diphosphine ligands and gold(III) compounds are described. These species exhibit luminescence which probably arises from a mixed ³LMMCT and ³MC excited state, and these properties may be useful for structural predictions in the solid state for the complexes which crystal structure have not been established.

Results and Discussion

Synthesis and Spectroscopic Characterization. To prepare the gold-selenolate complexes we have used two

different sources of the selenolate ligand, both prepared *in situ* in anhydrous THF and under argon atmosphere: the lithium salt, $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]\text{Li}$, obtained from $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4]\text{Li}$ and elemental selenium, and the potassium salt, $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]\text{K}$, obtained by cleavage of the selenium–selenium bond in $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4]_2\text{Se}_2$ with K-selectride, $\text{KB}[\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5]_3\text{H}$ (1:2 molar ratio). In some cases both sources work well in the preparation of the metal derivatives but for some compounds one of them gives better results; therefore, the best synthesis procedure is being described for a particular compound. The gold(I) complexes with a tertiary phosphine $[\text{Au}\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}(\text{PPh}_3)]$ (**1**) and $[\text{Au}\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}(\text{PPh}_2\text{py})]$ (**2**) were prepared from equimolar amounts of $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]\text{Li}$ or $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]\text{K}$ with the corresponding $[\text{AuCl}(\text{PR}_3)]$ precursor, respectively (see Scheme 1). Compounds $[\text{Au}_2\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2(\mu\text{-dppm})]$ (**3**) and $[\text{Au}_2\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2(\mu\text{-dppf})]$ (**5**) were obtained by the reaction of $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]\text{K}$ with $[\text{Au}_2\text{Cl}_2(\mu\text{-dppm})]$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) or $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$ [dppf = 1,1'-Fe-($\text{C}_5\text{H}_4\text{PPh}_2$)₂], respectively, in a 2:1 molar ratio. The reaction of $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]\text{Li}$ with $[\text{Au}_2\text{Cl}_2(\mu\text{-dppe})]$ (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) (2:1 molar ratio), in anhydrous THF and under argon atmosphere, afforded the isolation of the complex $[\text{Au}_2\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2(\mu\text{-dppe})]$ (**4**). Finally, the gold(III) derivative $\text{Bu}_4\text{N}[\text{Au}(\text{C}_6\text{F}_5)_3\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}]$ (**6**) was prepared from equimolar amounts of $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]\text{K}$ and $\text{Bu}_4\text{N}[\text{AuBr}(\text{C}_6\text{F}_5)_3]$.

All compounds were isolated as white to yellow or yellow-orange (**4**) solids and their formulation was supported by elemental analysis, mass spectrometry, and multinuclear (¹H, ¹³C, ¹⁹F, ³¹P, and ⁷⁷Se) NMR spectroscopy. The mass spectra of the complexes show the molecular peak for **1** at m/z = 674 (100%) and **3** at m/z = 1205 (16%). The spectra of complexes **4** and **5** do not present the molecular peak but high intensity $[\text{M-SeR}]^+$ fragments were observed, that is, m/z = 1006 (60%) for **4** and 1162 (100%) for **5**, respectively. The spectrum of **6** shows the $[\text{M-NBu}_4]^+$ as the base peak at m/z = 912.

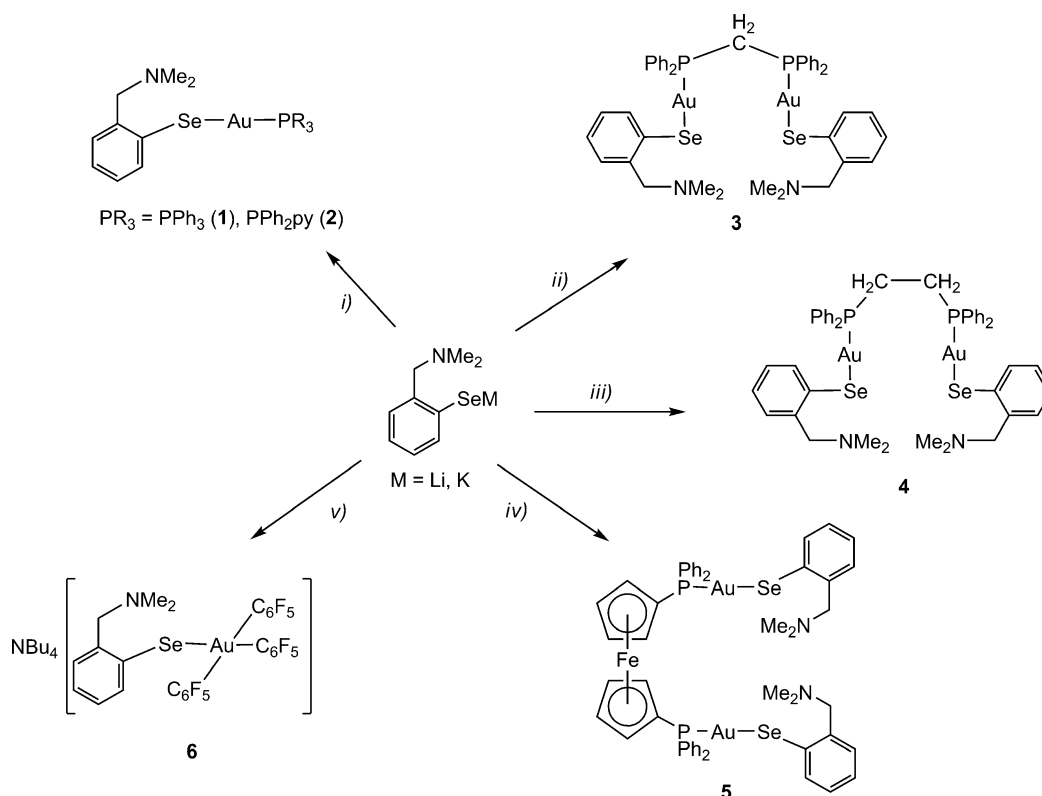
The NMR spectra for all the compounds were recorded in CDCl_3 , at room temperature. The assignment of the ¹H and ¹³C chemical shifts was made according to the numbering scheme shown in Scheme 2, on the basis of 2D (COSY, HMQC, HMBC) NMR experiments. The data are consistent with equivalence of the organic groups attached to selenium or to phosphorus in a molecular unit.

In the aliphatic region of the ¹H NMR spectra for all compounds **1–6** the resonances corresponding to the $-\text{CH}_2\text{NMe}_2$ group appear as singlets in the region δ 2.2–2.3 ppm for NMe₂ and δ 3.7–3.8 ppm $-\text{CH}_2\text{-N}$ protons. These resonances are similar to those found in the organic ligand ($\text{C}_6\text{H}_5\text{CH}_2\text{NMe}_2$: δ 2.24 and 3.40 ppm, respectively)¹⁵ and the oxidized form of the selenolate $[\text{2-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4]_2\text{Se}_2$ [δ 2.26 and 3.55 ppm, respectively].¹⁵ Although both aromatic protons from the selenolate fragment and the phenyl groups attached to the phosphorus atoms are expected to give

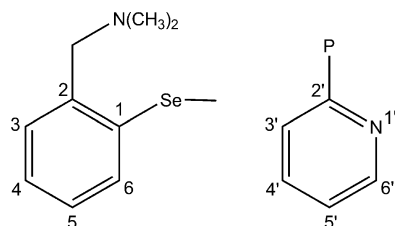
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Scheme 1. (i) $[\text{AuCl}(\text{PPh}_3)]$ or $[\text{AuCl}(\text{PPh}_2\text{py})]$, (ii) $[\text{Au}_2\text{Cl}_2(\mu\text{-dppm})]$, (iii) $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$, (iv) $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$, (v) $\text{Bu}_4\text{N}[\text{AuBr}(\text{C}_6\text{F}_5)_3]$



Scheme 2



resonances in a narrow frequency range, the aromatic region of the ^1H NMR spectra of the title complexes is generally very well resolved. The assignment of the multiplet resonances observed between δ 6.6 and 8.8 ppm was based on their integral ratio and multiplicity, and was confirmed by the 2D-COSY NMR spectrum. In addition, the ^1H NMR spectra of complexes **3–5** show a multiplet resonance for the methylene protons of the diphosphines in compounds **3** and **4** at 3.56 and 2.64 ppm, respectively, and two broad singlets for the α and β protons of the substituted cyclopentadienyl rings in compound **5** at 4.18 and 4.52 ppm, respectively.

In the ^{13}C NMR spectra the shielded resonance for $-\text{CH}_2-\text{NMe}_2$ pendant arm was assigned in the region δ 45.48–45.80 ppm for NMe_2 and δ 64.41–65.20 ppm for $-\text{CH}_2-\text{N}$. The assignment of the resonances in the aromatic region of the ^{13}C NMR spectrum, although apparently complicated by the number of different carbons for which resonances are expected and by the phosphorus–carbon couplings, was successfully resolved on the basis of 2D NMR experiments.

The room-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes **1–5** exhibit a singlet resonance at 36.7 (**1**), 37.0 (**2**), 29.4 (**3**), 36.2 (**4**), and 32.8 (**5**) ppm. The ^{77}Se NMR spectra also contain only one singlet resonance regardless the mono- or dinuclear nature of the complexes at 118.5 (**1**), 120.3 (**2**), 161.3 (**3**), 125.2 (**4**), 424.2 (**5**), and 205.9 (**6**) ppm. This behavior is consistent with the equivalence, in solution, at the NMR time scale, of the phosphorus atoms and selenium atoms, respectively, in the molecular unit of compounds containing diphosphine ligands.

For the gold(III) derivative **6** the ^{19}F NMR spectrum exhibits a typical pattern for a square planar geometry of the complex anion, that is, two sets of resonances in a 2:1 intensity ratio for the *trans* and *cis* pentafluorophenyl groups, respectively.

Crystal Structure Determinations. Single crystals of **4** and **5** were obtained from methylene dichloride/*n*-hexane (1:5 by volume) and acetone/*n*-hexane (1:5 by volume), respectively. The molecular structures with the atom numbering scheme are shown in Figures 1 and 2. Selected interatomic distances and angles are listed in Tables 1 and 2, respectively.

Although both compounds belong to the same class, that is, dinuclear gold complexes with a bridging diphosphine ligand, and there are some common structural features, their overall structure is completely different. In both compounds the gold atoms are primary dicoordinated, with almost linear $\text{Se}-\text{Au}-\text{P}$ fragments [$\text{Se}(1)-\text{Au}(1)-\text{P}(1)$ $173.16(5)^\circ$ in **4**, and $\text{Se}(1)-\text{Au}(1)-\text{P}(1)$ $177.96(2)^\circ$, $\text{Se}(2)-\text{Au}(2)-\text{P}(2)$ $170.61(2)^\circ$] in **5**. The deviation from the linearity observed for the coordination geometry at

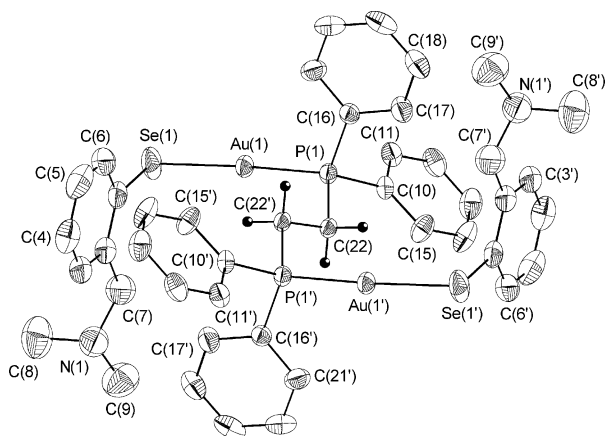


Figure 1. Structure of **4** showing the atom numbering scheme. Displacement parameter ellipsoids represent 30% probability surfaces. Hydrogen atoms, other than those of the ethylene bridge, are omitted for clarity.

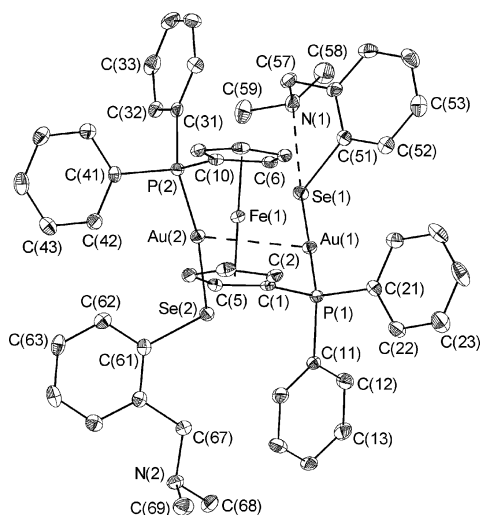


Figure 2. Structure of **5** showing the atom numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. Hydrogen atoms are omitted for clarity.

Table 1. Important Interatomic Distances (Å) and Angles (deg) for $[\text{Au}_2\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2(\mu\text{-dppe})]$ (**4**)

Au(1)–Se(1)	2.404(1)	Se(1)–Au(1)–P(1)	173.16(5)
Au(1)–P(1)	2.262(2)	P(1)–Au(1)–Au(1') ^a	105.98(5)
Au(1)···Au(1') ^a	3.0910(6)	Se(1)–Au(1)–Au(1') ^a	80.51(3)
Se(1)–C(1)	1.934(10)	C(1)–Se(1)–Au(1)	98.2(2)
P(1)–C(10)	1.807(7)	Au(1)–P(1)–C(10)	117.4(2)
P(1)–C(16)	1.806(8)	Au(1)–P(1)–C(16)	114.4(2)
P(1)–C(22)	1.820(6)	Au(1)–P(1)–C(22)	110.2(2)
N(1)–C(7)	1.431(15)	C(10)–P(1)–C(16)	104.1(3)
N(1)–C(8)	1.444(16)	C(10)–P(1)–C(22)	105.9(3)
N(1)–C(9)	1.475(15)	C(16)–P(1)–C(22)	103.7(3)
		C(7)–N(1)–C(8)	112.3(12)
		C(7)–N(1)–C(9)	110.2(11)
		C(8)–N(1)–C(9)	107.8(11)

^a Symmetry transformations used to generate equivalent atoms: "prime" ($2 - x, 1 - y, 1 - z$).

Au(2) atom is likely to be induced by the intramolecular Au(1)···Au(2) interaction (see subsequent discussion). In both complexes, the magnitude of the gold–phosphorus distances [2.262(2) Å in **4**; 2.2732(8)/2.2678(11) Å in **5**] is similar with those observed in the starting materials $[\text{Au}_2\text{Cl}_2(\mu\text{-dppe})]$ [2.242(6)/2.237(6) Å]¹⁶ and $[\text{Au}_2\text{Cl}_2(\mu\text{-$

Table 2. Important Interatomic Distances (Å) and Angles (deg) for $[\text{Au}_2\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2(\mu\text{-dppf})]$ (**5**)

Au(1)–Se(1)	2.4245(5)	Se(1)–Au(1)–P(1)	177.96(2)
Au(2)–Se(2)	2.4250(8)	Se(2)–Au(2)–P(2)	170.61(2)
Au(1)–P(1)	2.2732(8)	P(2)–Au(2)···Au(1)	103.18(2)
Au(2)–P(2)	2.2678(11)	P(1)–Au(1)···Au(2)	104.93(3)
Au(1)···Au(2)	3.0243(6)	Se(1)–Au(1)···Au(2)	74.22(2)
Se(1)–C(51)	1.926(3)	Se(2)–Au(2)···Au(1)	83.99(2)
Se(2)–C(61)	1.928(3)	C(51)–Se(1)–Au(1)	101.08(9)
P(1)–C(1)	1.802(3)	C(61)–Se(2)–Au(2)	101.73(9)
P(1)–C(11)	1.813(3)	Au(1)–P(1)–C(1)	113.90(9)
P(1)–C(21)	1.819(3)	Au(1)–P(1)–C(11)	111.67(10)
N(1)–C(57)	1.460(4)	Au(1)–P(1)–C(21)	115.48(10)
N(1)–C(59)	1.451(4)	C(1)–P(1)–C(11)	105.89(14)
N(1)–C(58)	1.456(4)	C(1)–P(1)–C(21)	103.45(13)
N(2)–C(67)	1.460(4)	C(11)–P(1)–C(21)	105.54(13)
N(2)–C(68)	1.456(4)	C(59)–N(1)–C(58)	111.4(3)
N(2)–C(69)	1.462(4)	C(59)–N(1)–C(57)	111.2(3)
		C(58)–N(1)–C(57)	111.2(3)

dppf)] [2.226(2) Å],¹⁷ as is that of the gold–selenium bonds in **4** [2.404(1) Å] and **5** [2.4245(5)/2.4250(8) Å] compared to $[\text{Au}_2(\text{SePh})_2(\mu\text{-dppe})]$ [2.4170(14)/2.4117(11) Å].⁹

The primary coordination geometry arising from the covalent bonds on selenium atoms is V-shaped in both compounds, with the C–Se–Au angles [98.2(2)° **4**; 101.08(9)/101.73(9)° in **5**] in the range observed in the related $[\text{Au}_2(\text{SePh})_2(\mu\text{-dppe})]$ derivative [94.9(3)–109.2(3)°].⁹ However, there are some differences to be noted. In the molecule of **4** the pendant arms from both organoselenolato ligands are twisted to bring the nitrogen atom far from both the selenium [non-bonding Se(1)···N(1) 4.61 Å] and the gold [non-bonding Au(1)···N(1) 5.66 Å] centers. By contrast, in the case of **5**, while the N(2) atom is not involved in any intra- or intermolecular interaction to selenium or gold atoms [non-bonding Se(2)···N(2) 4.579 Å, non-bonding Au(2)···N(2) 6.800 Å], the other nitrogen atom from the molecular unit is twisted toward the selenium atom with a short distance, 3.265 Å, that could be considered a weak intramolecular interaction [Se(1)···N(1) 3.265 Å, c.f. the sum of the van der Waals radii $\Sigma_{\text{vdW}}(\text{Se}, \text{N})$ ca. 3.54 Å],¹⁸ although packing forces may be also responsible. The vector of this interaction is placed *trans* to the Se–Au bond and thus the overall coordination around the Se(1) atom can be described as T-shaped.

Another important difference concerns the relative orientation of the AuSeR groups in the molecular unit. In **5** the gold atoms are close to each other and thus establish intramolecular gold–gold interactions [Au(1)···Au(2) 3.0243(6) Å, c.f. the sum of the van der Waals radii is $\Sigma_{\text{vdW}}(\text{Au}, \text{Au})$ ca. 3.4 Å].¹⁹ By contrast, in the molecular unit of **4**, the AuSeR moieties are placed in *trans* with respect to the P–C–C–P skeleton, thus preventing intramolecular gold–gold contacts. However, in the crystal of **4** intermolecular gold–gold short contacts are established [Au(1)···Au(1') 3.0910(6) Å] which result in a chain polymer association (Figure 3a) similar to that observed in the crystal of $[\text{Au}_2(\text{SePh})_2(\mu\text{-dppe})]$ [Au···Au 3.044(9) Å]⁹ (Figure 3b).

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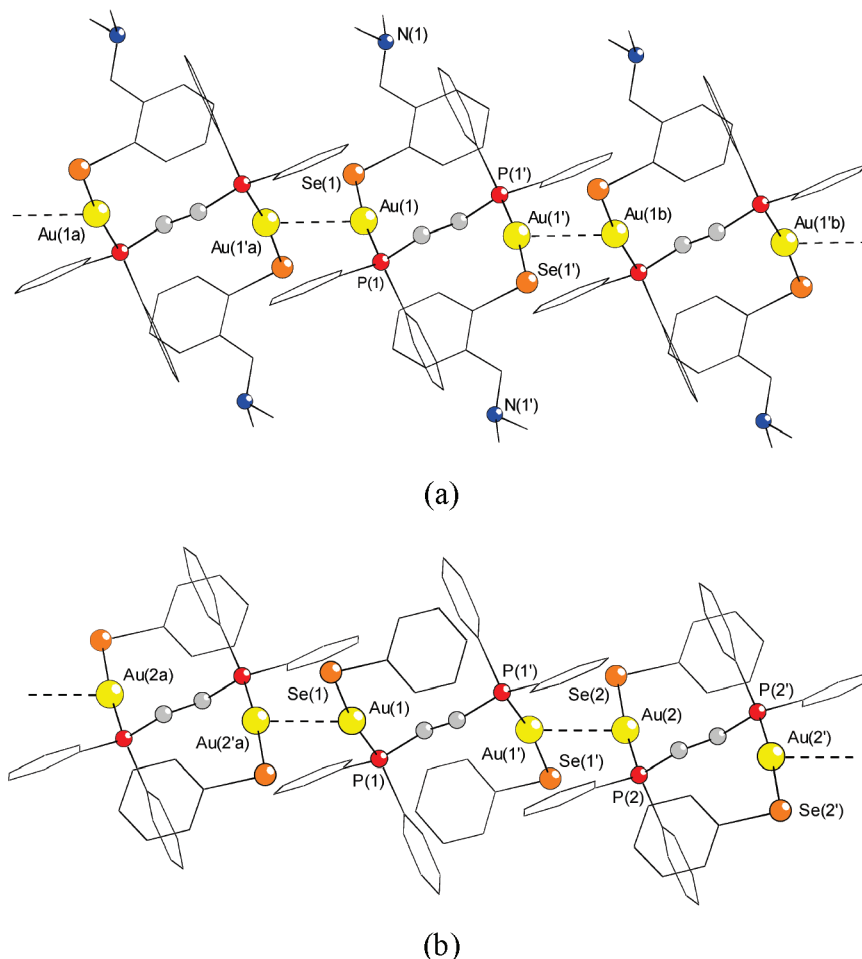


Figure 3. Chain polymer associations based on Au...Au contacts in the crystal of (a) $[\text{Au}_2\{\text{SeC}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\}_2(\mu\text{-dppe})]$ (**4**) [symmetry equivalent atoms $(2-x, 1-y, 1-z)$ and $(2-x, y, 0.5-z)$ are given by "prime" and "prime a", and (b) $[\text{Au}_2(\text{SePh})_2(\mu\text{-dppe})]$ [symmetry equivalent atoms $(-x, 1-y, -z)$ and $(-x, 1-y, 1-z)$ are given by "1 prime" and "2 prime"].⁹

UV Absorption and Diffuse-Reflectance Studies. The UV visible-absorption spectra in dichloromethane solutions, as well as the diffuse-reflectance ultraviolet spectra (DRUV) of solid samples, have been recorded for all complexes. In the solid state the compounds display similar spectra with broad absorptions from 220 to 450 nm (**1**, **3**, **4**, **6**), to 550 nm (**2**) or 500 (**5**). Nevertheless different profiles are obtained. For **1**, **2**, and **3** it consists just in one broadband. The profile of this band is more complicated for **4** and **5**. Thus, it is possible to distinguish two maxima at about 290 and 320 nm for **4**, and one maximum (ca. 320 nm) and a shoulder (ca. 450 nm) for **5**. Complex **6** displays two bands whose maxima appear at 290 and 380 nm, the latter being less intense. For comparison purposes we have studied the spectrum of $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Se}_2$ which is analogous to that found for **4**.

Absorption spectra in solution are analogous for all the complexes, and in all the cases different from that found in the solid state commented above. They consist in a sharp band with a maximum at 225 nm and a shoulder which decays up to 350–400 nm. Compound $[\text{2}-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Se}_2$ displays a different spectrum with

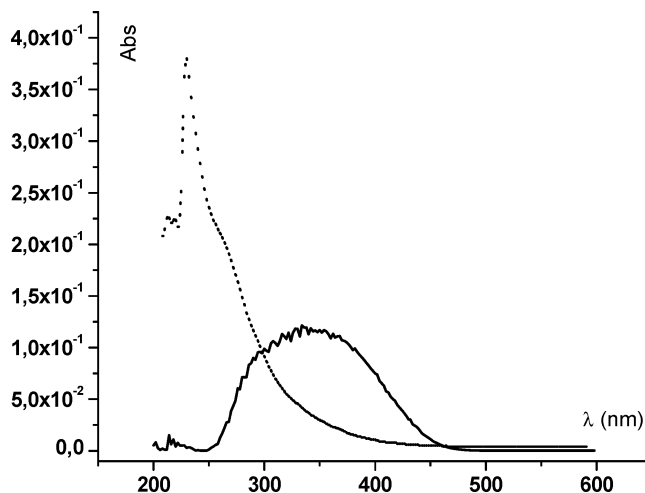


Figure 4. UV-absorption in 10^{-3} M dichloromethane solution (dotted) and diffuse-reflectance ultraviolet spectra (DRUV, solid line) spectra for complex **3**.

two intense maxima at about 225 and 290 nm. Thus, the main difference between the solid and the solution spectra consists of the absence of the absorptions in the 400–500 nm region when changing from solid samples to their liquid solutions. Figure 4 illustrates this behavior for compound **3**.

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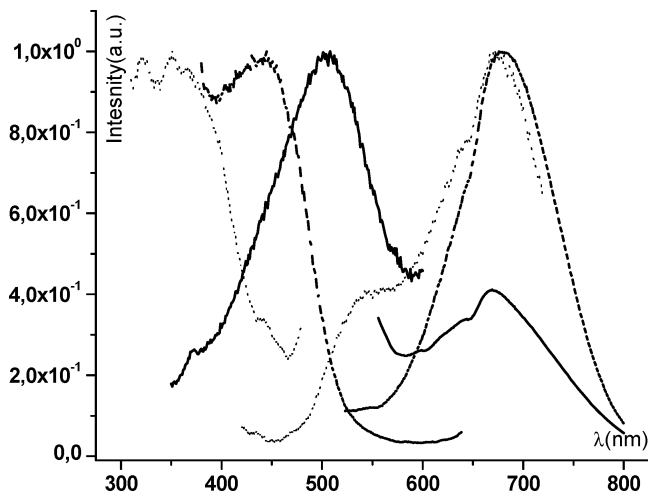


Figure 5. Emission (left) and excitation (right) spectra for compound **1** at room temperature (solid line) and 77 K (dotted line), excitation spectrum for $\lambda(\text{emission})$ 540 nm (thin line) and emission spectrum for $\lambda(\text{excitation})$ 330 nm (thin line); excitation spectrum for $\lambda(\text{emission})$ 680 nm (thick line) and emission spectrum for $\lambda(\text{excitation})$ 450 nm (thick line).

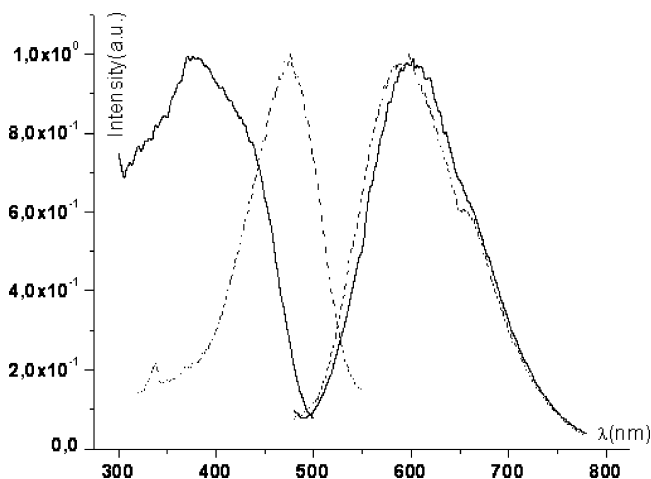


Figure 6. Emission (left) and excitation (right) spectra for compound **3** in the solid state at room temperature (dashed line) and 77 K (solid line).

Table 3. Emission Maxima [λ (nm)] for the Gold(I) Complexes **1–4**

compound	solid state, room temperature	77 K	frozen solution
1	675	550 ^a , 685	512
2	610, 700	570, 675	510
3	605	580	550
4	612	600	500, 605

^a Shoulder.

Luminescence Studies. The diselenide [2-(Me₂NCH₂)-C₆H₄]₂Se₂ is not luminescent, as well as the gold(III) complex **6**. The gold(I) complexes **1**, **2**, **3**, and **4** are emissive in the solid state, both at room temperature and at 77 K, and in frozen solution (see the representative Figures 5 and 6 and Table 3 for numerical data). Emissions in the solid state appear near 600 nm. These maxima appear, in general, at higher energies in dichloromethane frozen solutions. In some cases two bands (complexes **2** and **4**) or one band and a shoulder (compound **1**) are observed. No emission is observed for the ferrocene derivative **5**. This fact is not surprising, as ferrocene and its derivatives are known as good luminescence quenchers.²⁰

The origin of the luminescence in gold chalcogenolate derivatives has been related to charge transfer (³LMCT) processes from the chalcogenolate ligand to the gold center and/or to the presence of aurophilic interactions.^{3d,21} In mononuclear species ³LMCT transitions have been proposed as the origin of the luminescence, and the influence of the presence and strength of gold...gold intermolecular contacts in the emission energy has been studied.^{3a} In polynuclear complexes ³LMMCT transitions have been in many cases been proposed as the origin of the luminescence. In these cases the tuning of the aurophilic interactions leads frequently to modifications in the emissive properties. Emissions assigned to LMCT transitions have been described for diphosphine-bridged dinuclear gold(I) complexes with benzocrown-ether functionalized thiolate ligands²² or the polynuclear Au₁₆ ring, built from four tetranuclear “[dppm]Au₂(piperazine-1,4-dicarbodithiolate)Au₂(dppm)]²⁺” units.²³ MC and LMMCT transitions have been described as the origin of the emissions in the vapochromic compound [Au₂{S₂CN-(C₅H₁₁)₂}]₂, as the formation of linear Au...Au chains is induced by solvent molecules, and modifies its luminescent properties. Three bands are observed in the solid state at 77 K at 415, 456, and 560 nm. The emissions at higher energies have been attributed to ¹MC and ³MC transitions, respectively, and that at lower energy to ³LMMCT transitions.²⁴ This assignments are in agreement with the order in energies reported in Au(I) thiolate compounds for the filled non-bonding sulfur p orbital, considered to reside between the Au d_{z²}σ* (filled) and p_zσ (vacant). This order suggests that higher energies should be expected for MC transitions than for LMCT.²⁵ For compound [{Au(PPh₃)₂}(8-qnS)]BF₄ (8-qnS = quinoline-8-thiolate) the emission observed at 640 nm has been proposed to have a mixture of metal centered (MC) and LMCT (S→Au) origin.²⁶

Our complexes are emissive in the solid state and in frozen solutions (an intermediate situation between solid and solution state) and not in liquid solutions. Absorptions up to 400 nm are not present in solution, and no emission is observed in this media at room temperature. Thus, these absorptions may be related with the emissions observed. The presence of intermolecular gold...gold contacts has been confirmed for **4** and intramolecular Au...Au interactions are present in **5** (see X-ray studies). Aurophilic

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interactions can be expected for **1**, **2** (intermolecular), and **3** (inter and/or intramolecular). Such interactions should be weaker or even disappear in solution, and the data reveal that the emissive behavior of the complexes depends on the presence or the absence of Au...Au contacts. Thus (³MC) transitions could be the origin of the emissions but as commented above, from the energy ordering of the orbitals, higher energies than those observed could be expected for MC emissions in thiolate-gold complexes. Thus, taking into account this point and the presence of more than one band in some of the complexes, we propose that the excited-state character could be mainly ³LMMCT (S → Au...Au) mixed with some ³MC character. In complexes **1**, **2**, and **4** the shoulder (**1**) or band (**2** and **3**) at higher energies could be mainly ³MC in origin and, the band at lower energies mainly ³LMMCT in origin, although a mixing character could probable explain better the general behavior of these complexes.

The emissive properties of these complexes could be used to propose molecular aggregation. From the data above, the proposal of the formation of aggregates through aurophilic interactions for complexes **1**, **2**, and **3**, whose crystal structures have not been elucidated, seems reasonable.

Conclusions

Several selenolate gold(I) and gold(III) complexes with the organoselenolate ligand [2-(Me₂NCH₂)C₆H₄Se][−] have been prepared and are of the type [Au(SeR)(PR₃)], [Au₂(SeR)₂(μ-P-P)], or NBu₄[Au(C₆F₅)₃(SeR)]. The crystal structures revealed a different structural framework, that is, **4** crystallizes as a chain polymer with intermolecular aurophilic bonding, while **5** shows an intramolecular Au(I)...Au(I) interaction. We can conclude that, with the exception of the ferrocene derivative, which is not emissive, all the gold(I) complexes are luminescent in the solid state and frozen solution, but not in fluid solutions. Aurophilic interactions seem to play an important role in their emissive properties, which probably arise from a mixed ³LMMCT and ³MC excited state. Thus, the emission properties in these complexes seem to be useful for structural predictions and lead us to propose intermolecular aggregation in the solid state and frozen solution for the luminescence species **1**, **2**, **3**, and **4**. This point has been confirmed for the latter by X-ray studies.

Experimental Section

Instrumentation. C, H, N, and S analysis were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a Bruker Esquire 3000 Plus, with the electrospray (ESI) technique. Room-temperature NMR spectra in dried CDCl₃ for all the compounds, including 2D experiments, were recorded on a BRUKER ARX 400 spectrometer (¹H, 400 MHz, ¹³C, 100.6 MHz, ¹⁹F, 376.5 MHz, ³¹P, 161.9 MHz, and ⁷⁷Se, 76.4 MHz). The chemical shifts are reported in ppm relative to the residual peak of the deuterated solvent (ref CHCl₃: ¹H 7.26, ¹³C 77.0 ppm), and external standards: CFCl₃ (¹⁹F), H₃PO₄ 85% (³¹P) and Me₂Se (⁷⁷Se), respectively. The U.V. of dichloromethane solutions and diffuse-

reflectance UV (DRUV) spectra of solid samples were recorded with a Unicam UV-4 spectrophotometer. UV (DRUV) Spectra of solid samples were recorded using a Spectralon RSA-UC-40 Labsphere integrating sphere. The solid samples were mixed with dried KBr to form a homogeneous powder. The mixtures were placed in a homemade cell equipped with a quartz window. The intensities were recorded in Kubelka–Munk. Steady-state photoluminescence spectra were recorded with a Jobin–Yvon–Horiba fluorolog FL-3-11 spectrometer using band pathways of 3 nm for both excitation and emission.

Starting Materials. All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled prior to use. Selenium, butyllithium (15% in hexane), *N,N*-dimethylbenzylamine and Ag[O₃SCF₃] were commercially available. Other starting materials were prepared according to literature methods: [2-(Me₂NCH₂)C₆H₄]₂Li,²⁷ [2-(Me₂NCH₂)C₆H₄]₂Se₂,¹⁵ [AuCl(PPh₃)],²⁸ [AuCl(PPh₂py)],²⁹ [Au₂Cl₂(μ-dppe)],³⁰ [Au₂Cl₂(μ-dppm)],³¹ [Au₂Cl₂(μ-dppf)],³² and Bu₄N[AuBr(C₆F₅)₃].³³

Synthesis of [Au{SeC₆H₄(CH₂NMe₂)-2}(PPh₃)] (1**).** Elemental selenium (0.041 g, 0.52 mmol) was added to a solution of [2-(Me₂NCH₂)C₆H₄]₂Li (0.073 g, 0.52 mmol) in 50 mL of anhydrous THF, and the reaction mixture was stirred for 1 h at room temperature, under argon. The resulting yellow solution was treated (at −78 °C) with [AuCl(PPh₃)] (0.257 g, 0.52 mmol). After stirring for an additional 1 h the solvent was removed in vacuum, and the remaining solid was treated with methylene dichloride. The white LiCl was filtered off and the yellow solution was concentrated under reduced pressure until a solid deposited. The yellow product was recrystallized from methylene dichloride/*n*-pentane (1:5, v/v). Yield: 0.16 g (46%). Analytical data, Found: C, 48.13; H, 3.96; N, 1.99. Calcd for C₂₇H₂₇NPSeAu: C, 48.23; H, 4.05; N, 2.08. ¹H (CDCl₃, 400 MHz): δ 2.28 (6H, s, N-CH₃), 3.75 (2H, s, -CH₂-N), 6.90 (1H, dd, *H*₅, ³*J*_{HH} 7.2 Hz), 7.06 (1H, dd, *H*₄, ³*J*_{HH} 7.4 Hz), 7.33 (1H, d, *H*₃, ³*J*_{HH} 7.5 Hz), 7.48 (15H, m, P-C₆H₅), 7.99 (1H, d, *H*₆, ³*J*_{HH} 7.7 Hz). ¹³C (CDCl₃, 100.6 MHz): δ 45.75 (s, N-CH₃), 65.11 (s, -CH₂-N), 124.98 (s, *C*₄), 125.94 (s, *C*₅), 129.16 (d, P-C₆H₅-*meta*, ³*J*_{PC} 11.5 Hz), 129.68 (s, *C*₃), 131.68 (d, P-C₆H₅-*para*, ⁴*J*_{PC} 2.2 Hz), 133.02 (s, *C*₁), 134.11 (d, P-C₆H₅-*ortho*, ²*J*_{PC} 13.8 Hz), 137.92 (s, *C*₆), 141.00 (s, *C*₂); the resonance for the *ipso* carbons in PPh₃ were not observed. ³¹P (CDCl₃, 161.9 MHz): δ 36.7. ⁷⁷Se (CDCl₃, 76.4 MHz): δ 118.5.

Synthesis of [Au{SeC₆H₄(CH₂NMe₂)-2}(PPh₂py)] (2**).** A solution of KB[CH(CH₃)C₂H₅]₃H (K-selectride) 1 M (0.47 mL, 0.47 mmol) in THF was added to a solution of [2-(Me₂NCH₂)C₆H₄]₂Se₂ (0.1 g, 0.23 mmol) in 20 mL of anhydrous THF, and the reaction mixture was stirred for 4 h at room temperature, under argon. The resulting yellow solution with a white precipitate was treated dropwise (at −78 °C) with a solution [AuCl(PPh₂py)] (0.23 g, 0.46 mmol) in 20 mL of THF. After stirring for an additional 1 h the solvent was removed in vacuum, and the remaining solid was treated with acetone. The white KCl deposited and was filtered off. The yellow solution was concentrated under reduced pressure and

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precipitated with hexane. Yield: 0.20 g (63%). Analytical data, Found: C, 46.43; H, 3.81; N, 4.04. Calcd for $C_{26}H_{26}N_2SeAuP$: C, 46.37; H, 3.89; N, 4.16. 1H (CDCl₃, 400 MHz): δ 2.26 (6H, s, N-CH₃), 3.75 (2H, s, -CH₂-N), 6.93 (1H, ddd, H_5 , $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.5 Hz), 7.08 (1H, ddd, H_4 , $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.3 Hz), 7.34 [2H, m, H_3 + H_5' (PPy)], 7.40 (4H, m, P-C₆H₅-meta), 7.48 (2H, m, P-C₆H₅-para), 7.68 [5H, m, P-C₆H₅-ortho + H_4' (PPy)], 7.83 [1H, dd, H_3' (PPy), $^3J_{PH}$ 7.5, $^3J_{HH}$ 7.5 Hz], 7.99 (1H, dd, H_6 , $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.2 Hz), 8.74 [1H, dm, H_6' (PPy), $^3J_{PH}$ 4.7 Hz]. ^{13}C (CDCl₃, 100.6 MHz): δ 45.77 (s, N-CH₃), 65.16 (s, -CH₂-N), 125.04 [d, C_5' (PPy), $^4J_{PC}$ 2.0 Hz], 125.17 (s, C₄), 126.09 (s, C₅), 129.02 (d, P-C₆H₅-meta, $^3J_{PC}$ 11.5 Hz), 129.28 (d, P-C₆H₅-ipso, $^1J_{PC}$ 55.5 Hz), 129.42 (s, C₃), 130.95 [d, C_3' (PPy), $^2J_{PC}$ 31.6 Hz], 131.68 (d, P-C₆H₅-para, $^4J_{PC}$ 2.1 Hz), 132.71 (s, C₁), 134.45 (d, P-C₆H₅-ortho, $^2J_{PC}$ 13.8 Hz), 136.43 [d, C_4' (PPy), $^3J_{PC}$ 10.4 Hz], 137.90 (s, C₆), 141.01 (s, C₂), 151.19 [d, C_6' (PPy), $^3J_{PC}$ 15.2 Hz], 154.98 (d, C_2' (PPy), $^1J_{PC}$ 77.2 Hz). ^{31}P (CDCl₃, 161.9 MHz): δ 37.0. ^{77}Se (CDCl₃, 76.4 MHz): δ 120.3.

Synthesis of [Au₂{SeC₆H₄(CH₂NMe₂)-2}₂(μ -dppm)] (3). A solution of KB[CH(CH₃)C₂H₅]₃H (K-selectride) 1 M (0.56 mL, 0.56 mmol) in THF was added to a solution of [2-(Me₂NCH₂)C₆H₄]₂Se₂ (0.12 g, 0.28 mmol) in 20 mL of anhydrous THF, and the reaction mixture was stirred for 3 h at room temperature, under argon. The resulting yellow solution with white precipitate was treated dropwise (at -78 °C) with a solution of [Au₂Cl₂(μ -dppm)] (0.24 g, 0.28 mmol) in 20 mL of THF. After stirring for an additional 1 h the solvent was removed in vacuum, and the remaining solid was treated with acetone. The white KCl deposited and was filtered off. The yellow solution was concentrated under reduced pressure and precipitated with hexane. The yellow product was recrystallized from methylene dichloride/*n*-hexane (1:5, v/v). Yield: 0.25 g (75%). Analytical data, Found: C, 41.89; H, 2.06; N, 3.34. Calcd for C₄₃H₄₆N₂Se₂Au₂P₂: C, 42.87; H, 2.32; N, 3.84. 1H (CDCl₃, 400 MHz): δ 2.30 (12H, s, N-CH₃), 3.56 (2H, m, P-CH₂-P), 3.80 (4H, s, -CH₂-N), 7.49 (28H, m, -C₆H₄- + P-C₆H₅). ^{31}P (CDCl₃, 161.9 MHz): δ 29.4 (s, 2P). ^{77}Se (CDCl₃, 76.4 MHz): δ 161.3 (s, 2Se).

Synthesis of [Au₂{SeC₆H₄(CH₂NMe₂)-2}₂(μ -dppe)] (4). Elemental selenium (0.04 g, 0.50 mmol) was added to a solution of [2-(Me₂NCH₂)C₆H₄]₂Li (0.07 g, 0.50 mmol) in 50 mL of anhydrous THF, and the reaction mixture was stirred for 2 h at room temperature, under argon. The resulting yellow solution was treated with [Au₂Cl₂(μ -dppe)] (0.21 g, 0.25 mmol). After stirring for an additional 2 h the solvent was removed in vacuum, and the remaining solid was treated with methylene dichloride. The white LiCl deposited and was filtered off. The yellow-orange solution was concentrated under reduced pressure until a solid deposited. The yellow-orange product was recrystallized from methylene dichloride/*n*-hexane (1:5, v/v). Yield: 0.17 g (56%), mp 150 °C. Analytical data, Found: C, 43.20; H, 4.09; N, 2.26. Calcd for C₄₄H₄₈N₂P₂Se₂Au₂: C, 43.37; H, 3.97; N, 2.30. 1H (CDCl₃, 400 MHz): δ 2.27 (12H, s, N-CH₃), 2.64 (4H, s, br, -CH₂-CH₂-), 3.74 (4H, s, -CH₂-N), 6.86 (2H, ddd, H_5 , $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.2 Hz), 7.07 (2H, ddd, H_4 , $^3J_{HH}$ 7.4, $^4J_{HH}$ 0.9 Hz), 7.34 (2H, d, H_3 , $^3J_{HH}$ 7.5 Hz), 7.42 (8H, dd, P-C₆H₅-meta, $^3J_{HH}$ 7.3 Hz), 7.50 (4H, t, P-C₆H₅-para, $^3J_{HH}$ 7.2 Hz), 7.61 (8H, dd, P-C₆H₅-ortho, $^3J_{HP}$ 12.8, $^3J_{HH}$ 6.9 Hz), 7.94 (2H, dd, H_6 , $^3J_{HH}$ 7.7, $^4J_{HH}$ 0.8 Hz). ^{13}C (CDCl₃, 100.6 MHz): δ 24.18 (dd, P-CH₂-CH₂-P, $^1J_{PC}$ 18.3, $^2J_{PC}$ 18.3 Hz), 45.78 (s, N-CH₃), 65.20 (s, -CH₂-N), 125.12 (s, C₄), 126.00 (s, C₅), 129.47 (s, C₃), 128.93 (m, P-C₆H₅-ipso), 129.50 (m, P-C₆H₅-meta, $^3J_{PC}$ 11.2 Hz), 132.07 (s, P-C₆H₅-para), 132.82 (s, C₁), 133.20 (m, P-C₆H₅-ortho, $^2J_{PC}$ 13.8 Hz), 137.80 (s, C₆), 141.24 (s, C₂). ^{31}P (CDCl₃, 161.9 MHz): δ 36.2 (s, 2P). ^{77}Se (CDCl₃, 76.4 MHz): δ 125.2 (s, 2Se).

Synthesis of [Au₂{SeC₆H₄(CH₂NMe₂)-2}₂(μ -dppf)] (5). A solution of KB[CH(CH₃)C₂H₅]₃H (K-selectride) 1 M (0.47 mL, 0.47 mmol) in THF was added to a solution of [2-(Me₂NCH₂)C₆H₄]₂Se₂ (0.1 g, 0.23 mmol) in 20 mL of anhydrous THF, and the reaction mixture was stirred for 4 h at room temperature, under argon. The resulting yellow solution with white precipitate was treated (at -78 °C) with [Au₂Cl₂(μ -dppf)] (0.24 g, 0.23 mmol). After stirring for an additional 1 h the solvent was removed in vacuum, and the remaining solid was treated with methylene dichloride. The white KCl was filtered off, and the yellow solution was concentrated under reduced pressure, then precipitated with hexane. The yellow product was recrystallized from methylene dichloride/*n*-hexane (1:5, v/v). Yield: 0.25 g (80%). Analytical data, Found: C, 45.43; H, 3.81; N, 2.04. Calcd for C₅₂H₅₂Au₂FeN₂P₂Se₂: C, 45.58; H, 4.01; N, 2.03. 1H (CDCl₃, 400 MHz): δ 2.29 (12H, s, N-CH₃), 3.76 (4H, s, -CH₂-N), 4.18, 4.52 (8H, m, br, C₅H₄-ferrocene), 6.89 (2H, ddd, H_5 , $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.4 Hz), 7.06 (2H, ddd, H_4 , $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.2 Hz), 7.34 (2H, dd, H_3 , $^3J_{HH}$ 7.5, $^4J_{HH}$ 0.9 Hz), 7.39 (8H, m, P-C₆H₅-meta), 7.48 (12H, m, P-C₆H₅-ortho+para), 7.98 (2H, dd, H_6 , $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.0 Hz). ^{13}C (CDCl₃, 100.6 MHz): δ 45.80 (s, N-CH₃), 65.10 (s, -CH₂-N), 74.72 (m, C₅H₄-ferrocene), 125.09 (s, C₄), 125.90 (s, C₅), 128.91 (d, P-C₆H₅-meta, $^3J_{PC}$ 11.4 Hz), 129.24 (s, C₃), 131.41 (d, P-C₆H₅-ipso, $^1J_{PC}$ 15.9 Hz), 131.43 (s, P-C₆H₅-para), 132.91 (s, C₁), 133.47 (d, P-C₆H₅-ortho, $^2J_{PC}$ 14.1 Hz), 137.98 (s, C₆), 141.31 (s, C₂). ^{31}P (CDCl₃, 161.9 MHz): δ 32.8 (s, 2P). ^{77}Se (CDCl₃, 76.4 MHz): δ 424.2 (s, 2Se).

Synthesis of Bu₄N[Au(C₆F₅)₃{SeC₆H₄(CH₂NMe₂)-2}] (6). A solution of KB[CH(CH₃)C₂H₅]₃H (K-selectride) 1 M (0.28 mL, 0.28 mmol) in THF was added to a solution of [2-(Me₂NCH₂)C₆H₄]₂Se₂ (0.06 g, 0.14 mmol) in 20 mL of anhydrous THF, and the reaction mixture was stirred for 4 h at room temperature, under argon. The resulting yellow solution with white precipitate was treated (at -78 °C) with Bu₄N[AuBr(C₆F₅)₃] (0.28 g, 0.28 mmol). After stirring for an additional 2 h the solvent was removed in vacuum, and the remaining solid was treated with methylene dichloride. The white KBr deposited and was filtered off. The pale yellow solution was concentrated under reduced pressure and precipitated with hexane. The pale yellow product was recrystallized from methylene dichloride/*n*-hexane (1:5, v/v). Yield: 0.13 g (80%). Analytical data, Found: C, 45.03; H, 3.91; N, 2.34. Calcd for C₄₃H₄₈N₂SeAuF₁₅: C, 44.76; H, 4.19; N, 2.43. 1H (CDCl₃, 400 MHz): δ 0.99 (12H, t, CH₃CH₂CH₂CH₂-, $^3J_{HH}$ 7.3 Hz), 1.43 (8H, tq, CH₃CH₂CH₂CH₂-, $^3J_{HH}$ 7.4 Hz), 1.64 (8H, m, CH₃CH₂CH₂CH₂-), 2.27s (6H, N-CH₃), 3.16 (8H, m, CH₃CH₂CH₂CH₂-), 3.70 (2H, s, -CH₂-N), 6.67 (1H, ddd, H_5 , $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.3 Hz), 6.98 (1H, ddd, H_4 , $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.2 Hz), 7.12 (1H, dd, H_3 , $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.0 Hz), 7.31 (1H, d, H_6 , $^3J_{HH}$ 7.6 Hz). ^{13}C (CDCl₃, 100.6 MHz): δ 13.37 (s, CH₃CH₂CH₂CH₂-), 19.55 (s, CH₃CH₂CH₂CH₂-), 23.76 (s, CH₃CH₂CH₂CH₂-), 45.48 (s, N-CH₃), 58.79 (s, CH₃CH₂CH₂CH₂-), 64.42 (s, -CH₂-N), 115.60, 119.86 (m, C₆F₅), 125.13 (s, C₅), 126.29 (s, C₄), 128.12 (s, C₃), 131.19 (s, C₁), 135.70, 136.90, 138.18 (m, C₆F₅), 138.78 (s, C₆), 139.25 (m, C₆F₅), 142.75 (s, C₂), 143.80, 146.10 (m, C₆F₅). ^{19}F (CDCl₃, 376.48 MHz): δ -163.3 (4F, m, C₆F₅-meta), -162.9 (2F, m, C₆F₅-meta), -161.1 (2F, t, C₆F₅-para, $^3J_{FF}$ 19.9 Hz), -160.0 (1F, t, C₆F₅-para, $^3J_{FF}$ 20.1 Hz), -121.2 (2F, m, C₆F₅-ortho), -119.2 (4F, m, C₆F₅-ortho). ^{77}Se (CDCl₃, 76.4 MHz): δ 205.9.

Crystal Structure Determinations. Table 4 lists details for crystal and refinement data.

A block crystal of **4** was attached with epoxy glue on cryoloops, and data were collected at room temperature on a Bruker SMART APEX diffractometer, while for **5** a crystal was mounted in inert oil on glass fiber and transferred to the cold

Table 4. Details of Data Collection and Structure Refinement for **4** and **5**

compound	4	5
chemical formula	C ₄₄ H ₄₈ Au ₂ N ₂ P ₂ Se ₂	C ₅₈ H ₆₆ Au ₂ FeN ₂ O ₂ P ₂ Se ₂
crystal habit	prism	prism
cryst size (mm ³)	0.41 × 0.19 × 0.11	0.40 × 0.22 × 0.20
cryst syst	monoclinic	monoclinic
space group	C2/c	P2(1)/c
<i>a</i> (Å)	24.963(2)	16.809(3)
<i>b</i> (Å)	10.7223(9)	14.032(3)
<i>c</i> (Å)	16.3611(14)	23.316(5)
α (deg)	90.00	90.00
β (deg)	95.532(2)	95.50(3)
γ (deg)	90.00	90.00
<i>U</i> (Å ³)	4358.8(6)	5474.0(19)
<i>Z</i>	4	4
<i>D</i> _{calcd} (g cm ⁻³)	1.857	1.811
<i>M</i>	1218.6	1492.77
<i>F</i> (000)	2328	2904
<i>T</i> (°C)	24(2)	−173(2)
2 θ _{max} (deg)	50	50
μ (Mo K α) (mm ⁻¹)	8.499	7.040
transmission	0.4549, 0.1283	0.3333, 0.1651
no. of reflns measured	22845	73151
no. of unique reflns	4459	9571
<i>R</i> _{int}	0.0545	0.0286
<i>R</i> ₁ (<i>F</i> ² > 2 σ (<i>F</i> ²))	0.0503	0.0181
<i>wR</i> ₂	0.1013	0.0373
no. of reflns used	4459	9571
no. of restraints	0	0
no. of parameters	237	646
goodness-of-fit on <i>F</i> ²	1.234	1.116
largest diff. peak and hole (e Å ⁻³)	1.555, −1.499	0.597, −0.389

gas stream of a Xcalibur Oxford Diffraction diffractometer equipped with a low-temperature attachment. For both compounds data were collected using monochromated Mo K α radiation ($\lambda = 0.71073$ Å). For **4** data reduction was performed

using the SAINT software,³⁴ and the data were corrected for Lorentz polarization and absorption effects using the SAINT, SADABS, and SORTAV programs.³⁵ For **5** data reduction was performed with the program Crystallis RED, and absorption correction based on multiple scans was applied with the program SADABS.³⁴ The structures were refined on *F*² using the program SHELXL-97.³⁶ All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The drawings were created with the DIAMOND program.³⁷

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **4** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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