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Coordination studies of the ferrocenyl phosphine selenide ligand $FcCON(CH_2CH_2PPh_2Se)_2$

Silvia Canales, M. Dolores Villacampa, Antonio Laguna, M. Concepción Gimeno*

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC – Universidad de Zaragoza, E-50009 Zaragoza, Spain

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A B S T R A C T

The oxidation of the ferrocenyl phosphine ligand $FcCON(CH_2CH_2PPh_2)_2$ with elemental selenium leads to the synthesis of the ferrocenyl phosphine selenide $FcCON(CH_2CH_2PPh_2Se)_2$ (**L1**). The coordination chemistry of this ligand with group 11 metals and palladium has been studied, and several complexes with coordination of the metal to the selenium atoms have been prepared. The ligand **L1** reacts with pentafluorophenyl gold(I) or gold(III) species leading to the complexes $[\{Au(C_6F_5)\}_2(\mu\text{-L1})]$ or $[\{Au(C_6F_5)_3\}_2(\mu\text{-L1})]$, respectively. The reaction of two equivalents of **L1** with silver(I) or copper(I) salts gives the tetra-coordinate complexes $[M(L1)_2]X$ (M = Cu, X = PF_6; Ag, X = OTf), or with *trans*-$[PdCl_2(NCPh)_2]$ affords the square planar palladium derivative $[PdCL_2(L1)]$. The ligand **L1** and the gold(I) complex $[\{Au(C_6F_5)\}_2(\mu\text{-L1})]$ have been characterized by X-ray diffraction.

1. Introduction

Ferrocene is a very attractive and versatile molecule with important properties such as high electron density, aromaticity and redox reversibility. These characteristics, together with the well established routes to mono and 1,1′-disubstituted ferrocene derivatives with a great variety of organic fragments containing donor atoms such as O, N, S, P, make ferrocene a very suitable building block in many fields of research [1–3]. These functionalized ferrocene derivatives and its metal complexes represent an important topic of research in many areas that seek special properties of such species, e.g. non-linear optical properties, charge transport, liquid crystals, electrochemical recognition, catalysis, nanoparticles, immunoassay reagents or biological applications [1–12].

Ferrocene phosphines have been thoroughly studied as represented for the well-known 1,1′-bis(diphenylphosphine)ferrocene (dppf) [1]. We have described the formation of several amidephosphines containing ferrocene units, studied their coordination chemistry [13] and also showed that some gold and silver complexes are active as antitumoral agents [14]. However phosphine chalcogenides are not well studied in coordination chemistry although some metal complexes can serve as excellent precursors of semiconductor materials [15]. In particular phosphine–selenide complexes have been little studied in general and also in group 11 metal chemistry, in spite of these metals, especially gold, form strong bonds with the selenium atom. Only a few reports have dealt with the coordination of gold and silver to $SePR_3$ [16], dppmSe (dppm = bis(diphenylphosphino)methane) [17], SedppmSe [18], SedppfSe [19] or $SePPh_2NPPh_2Se^-$ or $SePPh_2NHPPh_2Se$ [20]. With the aim of studying group 11 complexes with ferrocenyl selenide phosphines, which may have interest as precursors of metal selenides as well as biologically relevant gold complexes, here we report on the synthesis of the ligand and the study of its coordination chemistry towards group 11 and palladium metals.

2. Results and discussion

The ferrocenyl phosphino-amide ligand $FcCON(CH_2CH_2PPh_2)_2$ has been previously described by us by reaction of chlorocarbonylferrocene with the amino-phosphine $N(CH_2CH_2PPh_2)_2$ in dichloromethane, and in the presence of triethylamine [14]. The reaction of this phosphine-amide with elemental selenium gives the ferrocenyl phosphine selenide ligand $FcCON(CH_2CH_2PPh_2Se)_2$ (**L1**) as an orange air and moisture stable solid (see Equation (1)).

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* Corresponding author.
E-mail address: gimeno@unizar.es (M.C. Gimeno).

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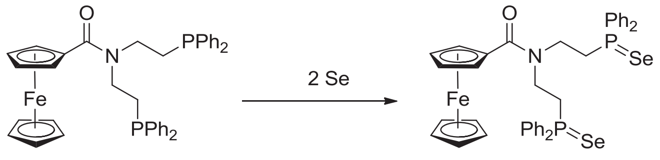


L1

Equation 1. Synthesis of the ligand **L1**.

The IR spectrum shows in addition to the absorptions arising at the ferrocenyl and phosphine units, the ν(C═O) vibration at 1627 cm^{-1} and the new ν(P═Se) vibration at 535 cm^{-1}. In the ^{31}P {^{1}H} NMR spectrum two resonances appear at 32.4 and 27.8 ppm, indicating the inequivalence of the phosphorus atoms, these two resonances have selenium satellites with J(PSe) of 743 and 737 Hz, respectively, corroborating the coordination of the phosphorus atoms to selenium. The ^{1}H NMR spectrum shows two multiplets for the α and β protons of the substituted cyclopentadienyl ring and a singlet for the unsubstituted cyclopentadienyl moiety. The resonances for the methylene protons appear as two broad multiplets, indicating that these protons have a close chemical shift. In the mass spectrum (LSIMS$^+$) the molecular peak at m/z = 811 (60%) appears.

The ligand **L1** has been characterized by X-ray diffraction studies and the molecule is shown in Fig. 1. The nitrogen atom of the amide is found in a trigonal planar coordination with angles of C(11)—N(1)—C(12) 127.6(7)°, C(11)—N(1)—C(14) 115.9(7)° and C(12)—N(1)—C(14) 116.1(7)°. The N—C distance to the amide carbon is C(11)—N(1) 1.372(10) Å. The P═Se bonds are Se(1)—P(1) 2.107(2) and Se(2)—P(2) 2.097(3) Å, which agrees with a double bond P═Se. The C═O unit points out to one of the phosphine arms, which can be the reason that both phosphorus becomes inequivalent in solution.

The reaction of **L1** with [Au(C_6F_5)(tht)] in a 1:2 molar ratio gives the complex of stoichiometry [{Au(C_6F_5)}$_2$(μ-L1)] (**1**) (see Scheme 1) as an orange solid. The IR spectrum for this compound shows the absorptions arising at the vibrations of the pentafluorophenyl rings at 1500 (vs), 954 (s) and 800 (m) cm^{-1}. The ν(C═O) and ν(C═N) vibrations around 1640 and 1587 cm^{-1} are also present. The ^{1}H NMR spectra show several resonances for the different protons in the molecule: a singlet for the protons of the unsubstituted cyclopentadienyl ring at 4.22 ppm, two multiplets for the α and β protons of the substituted cyclopentadienyl ring at 4.36 and 4.75 ppm, two multiplets for the methylene protons at 3.03 and 3.89 ppm of the phosphine ligands, and several multiplets for the phenylic protons. The ^{31}P{^{1}H} NMR spectrum presents two resonances for the inequivalent phosphorus atoms at 30.6 and 26.8 ppm with selenium satellites and coupling constants of J(PSe) of 552 and 551 Hz, respectively. The ^{19}F NMR spectrum of **1** presents two multiplets for the equivalent *ortho* and *meta* fluorine at −160.0 and −116.5, respectively, and other multiplet at −162.5 for the *para* fluorine. In this case the pentafluorophenyl rings appear as equivalent, although the phosphorus atoms are not, and this is probably because there is a higher degree of rotation around the bond Au—C_6F_5. The LSIMS$^+$ mass spectrum shows the molecular peak at m/z = 1541 (25%) and the fragment arising at the lost of one pentafluorophenyl ring at m/z = 1370 (15%).

The crystal structure of complex **1** has been established by X-ray diffraction studies and the molecule is shown in Fig. 2. The gold atoms are in a linear geometry, slightly distorted, with angles of C(41)—Au(1)—Se(1) 178.78(19)° and C(71)—Au(2)—Se(2) 175.32(18)°. The Au—C distances are Au(1)—C(41) 2.007(7) and Au(2)—C(71) 2.023(7) Å, which are of the same order and similar to other complexes with pentafluorophenyl rings bonded to gold(I). The Au—Se bond distances are Au(1)—Se(1) 2.4227(7) and Au(2)—Se(2) 2.4145(8) Å, which are also of the same order than those found in complexes with Au—Se═P bonds such as [Au(SedppfSe)][AuCl$_2$] (Au—Se 2.4000(9)—2.4217(8) Å) [19a]. The P—Se distances are P(1)—Se(1) 2.1686(18) and P(2)—Se(2) 2.1633(18) Å, which are longer than those in the starting ligand **L1**, as expected after the coordination of the gold atoms.

The treatment of **L1** with the gold(III) compound [Au(C_6F_5)$_3$(tht)] in a molar ratio 1:2 gives the gold(III) species [{Au(C_6F_5)$_3$}$_2$(μ-L1)] (**2**), where the gold centres are coordinated to the selenium atoms. The IR spectrum presents, apart from other absorptions, the vibrations due to the pentafluorophenyl groups bonded to gold(III) at 1505(s), 996(s), 805(s) and 795(s) cm^{-1}. The ^{31}P{^{1}H} NMR spectrum presents one broad singlet at room temperature indicating that both phosphorus are equivalent, however at −55 °C there are two singlets because the phosphorus becomes inequivalent. The ^{1}H NMR spectrum shows the expected resonances for the ferrocenyl phosphine ligand, with a different chemical shift. In the ^{19}F NMR spectrum of **2** several resonances appears; usually the three C_6F_5 groups attached to the gold atom give two different ^{19}F sets of resonances in a 1:2 ratio for the non-equivalent C_6F_5 groups (one of them *trans* to selenium and the other two *trans* each other, respectively). In complex **2** both "Au(C_6F_5)$_3$" are inequivalent and then up to twelve resonances should appear, but in this case some of the resonances are overlapped. In the mass spectrum (LSIMS$^+$) the molecular peak does not appears but it does the fragment arising at the lost of a Au(C_6F_5)$_3$ fragment at m/z = 1512 (40%).

The reaction of the ligand **L1** with [Cu(NCMe)$_4$]PF$_6$ or AgOTf in a 2:1 molar ratio affords the tetra-coordinated complexes [M(L1)$_2$]X (M = Cu, X = PF$_6$ (**3**); Ag, X = OTf (**4**)). Complexes **3** and **4** are orange solids and behave as 1:1 electrolytes in acetone solutions. The IR spectra show the absorptions for the anion PF$_6$ in **3** at 844 (s) cm^{-1} and those for the trifluoromethanesulphonate at 1265 (vs, br) [ν_{as}(SO$_3$)], 1223 (s) [ν_s(CF$_3$)], 1150 (vs, br) [ν_{as}(CF$_3$)] and 1023 (s) [ν_s(SO$_3$)] cm^{-1} in **4**. The ^{31}P{^{1}H} NMR spectrum of **3** shows a broad singlet at room temperature with a J(PSe) of 655 Hz; however at −55 °C the resonance splits into three singlets in an approximate ratio 1:2:1, which indicates the inequivalence of all the phosphorus atoms, but two of the resonances are overlapped because the close chemical shift. In the ^{1}H NMR spectrum also broad resonances

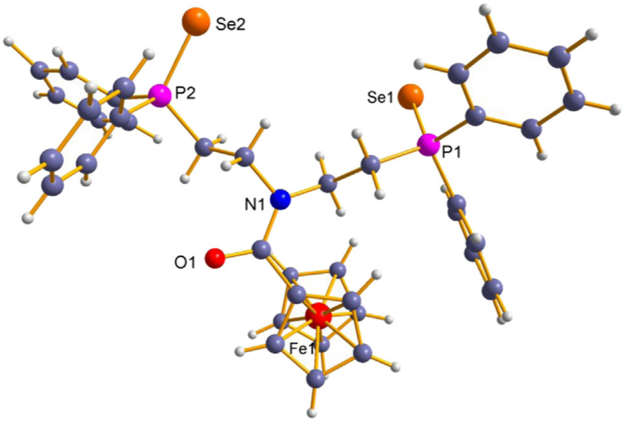
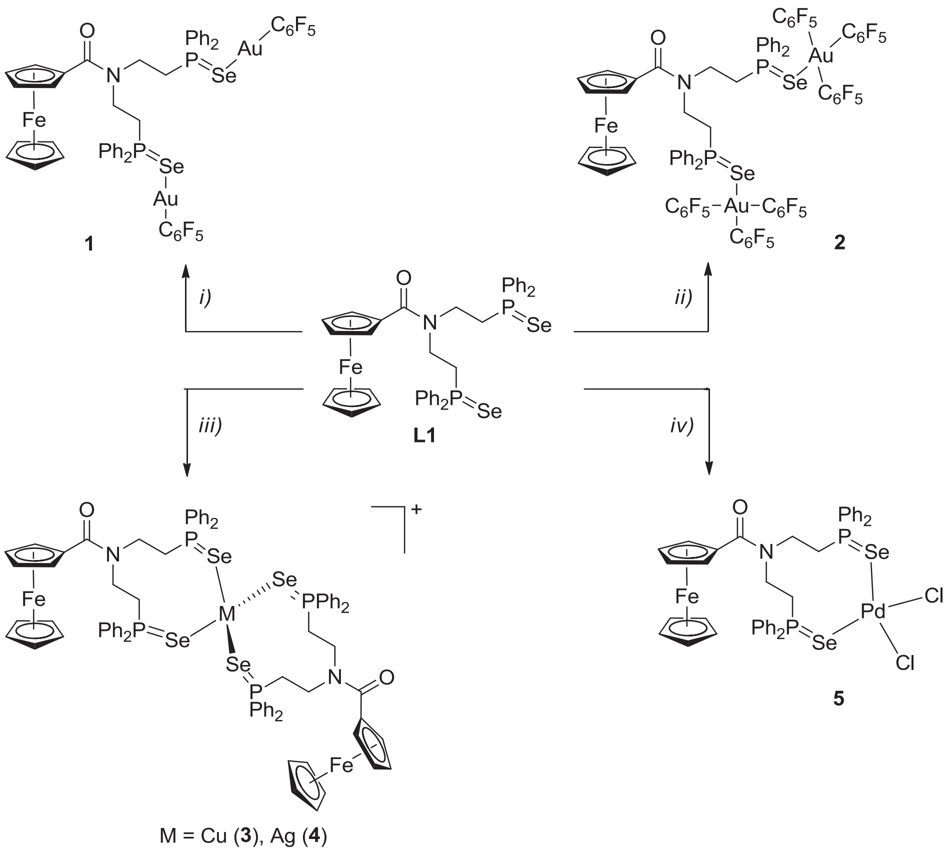


Fig. 1. Molecular structure of the compound **L1**, with the atom labelling scheme. Selected bond lengths (Å) and angles (°): Se(1)—P(1) 2.107(2), Se(2)—P(2) 2.097(3), N(1)—C(11) 1.372(10), N(1)—C(12) 1.462(9), N(1)—C(14) 1.474(9), O(1)—C(11) 1.228(9); C(11)—N(1)—C(12) 127.6(7), C(11)—N(1)—C(14) 115.9(7), C(12)—N(1)—C(14) 116.1(7), C(31)—P(1)—Se(1) 113.4(3), C(13)—P(1)—Se(1) 112.3(3), C(21)—P(1)—Se(1) 113.5(3), C(15)—P(2)—Se(2) 113.7(3), C(61)—P(2)—Se(2) 113.2(2), C(51)—P(2)—Se(2) 113.1(2), C(41)—P(2)—Se(2) 114.1(3).

6



Scheme 1. Synthesis of the metal complexes: i) 2[Au(C_6F_5)(tht)], ii) 2[Au(C_6F_5)$_3$(tht)], iii) ½[Cu(NCMe)$_4$]PF_6 or ½Ag(OTf), iv) *trans*-[$PdCl_2$(NCPh)$_2$].

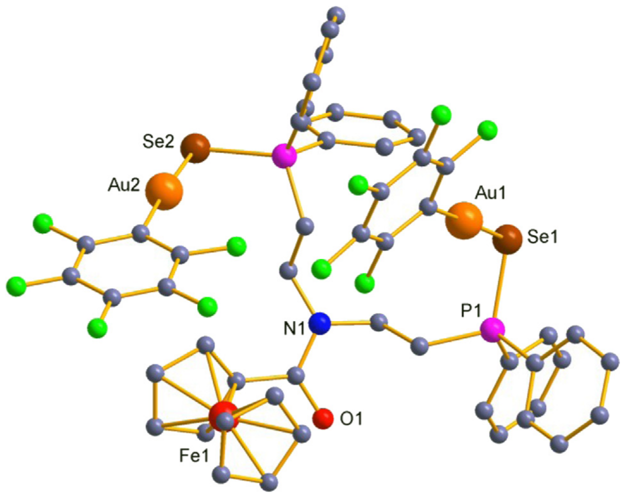


Fig. 2. Molecular structure of complex **1** in the crystal showing the atom labelling scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–C(41) 2.007(7), Au(1)–Se(1) 2.4227(7), Au(2)–C(71) 2.023(7), Au(2)–Se(2) 2.4145(8), P(1)–Se(1) 2.1686(18), P(2)–Se(2) 2.1633(18), C(11)–O(1) 1.243(7), C(11)–N(1) 1.359(7), N(1)–C(12) 1.460(7), N(1)–C(14) 1.462(7) Å; C(41)–Au(1)–Se(1) 178.78(19), C(71)–Au(2)–Se(2) 175.32(18), P(1)–Se(1)–Au(1) 93.58(5), P(2)–Se(2)–Au(2) 93.34(5), C(11)–N(1)–C(12) 116.5(5), C(11)–N(1)–C(14) 125.0(5), C(12)–N(1)–C(14) 115.5(5)°.

appear as one broad signal for all the ferrocene protons, two multiplets for the methylene protons and a multiplet for the phenylic protons. At −55 °C the ferrocene protons appear as the typical singlet for the unsubstituted ferrocene and two multiplets for the substituted ferrocene protons, but the methylene protons now only one broad multiplet appears. The $^{31}P\{^1H\}$ NMR spectrum of **4** also shows a broad singlet at room temperature with a *J*(PSe) of 653 Hz and at −55 °C the resonance widens but does not resolve. The ^1H NMR spectrum is similar at both temperatures and the typical resonances for the ligand appear. The mass spectra (LSIMS$^+$) show the cation molecular peaks at $m/z = 876$ (100%) for **3** and 920 (55%) for **4**.

The reaction of **L1** with *trans*-[$PdCl_2$(NCPh)$_2$] in a 1:1 molar ratio leads, after the displacement of the benzonitrile ligands, to the formation of complex [$PdCl_2$L1] (**5**). Complex **5** is a red solid, stable to air and moisture, that behaves as non-conductor in acetone solutions. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows two singlets at 34.5 and 30.0 ppm. The ^1H NMR spectrum presents two multiplets for the methylene protons, a singlet for the protons of the unsubstituted Cp ring, two multiplets for the protons of the substituted Cp ring and the multiplets due to the phenylic protons. The mass spectrum does not show the molecular ion peak but the fragment [PdL1]$^+$ appears at $m/z = 918$ (5%).

3. Conclusions

The ferrocenyl phosphine selenide ligand FcCON($CH_2CH_2PPh_2Se$)$_2$ (**L1**) has been prepared by oxidation of the ferrocenyl phosphine

$FcCON(CH_2CH_2PPh_2)_2$ with elemental selenium. The crystal structure revealed that both arms of the phosphine selenide ligand are not equivalent because the C=O bond points out to one of them. Several gold(I), gold(III), silver(I), copper(I) and palladium complexes have been synthesized with this ligand of different stoichiometries, showing than the phosphine selenide coordinates as bridging or chelating ligand. The crystal structure of the gold(I) species $[\{Au(C_6F_5)\}_2(\mu\text{-L1})]$ (**1**) showed that the gold centres coordinate to the selenium atoms and an elongation of the P=Se bond lengths takes place.

4. Experimental

4.1. Instrumentation

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. C, H, N and S analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the liquid secondary-ion mass spectra (LSIMS) technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on Bruker ARX 300 and Bruker ARX 400 spectrometers in $CDCl_3$, otherwise stated. Chemical shifts are cited relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external) and 85% H_3PO_4 (^{31}P, external).

4.2. Starting materials

The starting materials $FcCON(CH_2CH_2PPh_2)_2$ [14], $[Au(C_6F_5)(tht)]$ [21], $[Cu(NCMe)_4]PF_6$ [22] were prepared according to published procedures. All other reagents were commercially available.

*4.3. Synthesis of $FcCON(CH_2CH_2PPh_2Se)_2$ (**L1**)*

To a solution of $FcCON(CH_2CH_2PPh_2)$ (0.653 g, 1 mmol) in tetrahydrofurane (20 mL) was added selenium powder (0.158 g, 2 mmol) and the mixture was stirred for 8 h. Evaporation of the solvent to ca. 5 mL and addition of hexane (10 mL) gave ligand **L1** as an orange solid. **L1**: Yield 85%, 689 mg. Λ_M 1.3 Ω^{-1} cm^2 mol^{-1}. $C_{39}H_{37}FeNOP_2Se_2$ (811.43): calcd. C 57.73, H 4.60, N 1.73; found C 57.32, H 4.56, N 1.77. ^1H NMR, δ: 3.03 (m, 4H, CH_2), 3.89 (m, 4H, CH_2), 4.22 (s, 5H, C_5H_5), 4.36 (m, 2H, C_5H_4), 4.75 (m, 2H, C_5H_4), 7.15–7.85 (m, 20H, Ph). $^{31}P\{^1H\}$, δ: 32.4 (s, 1P, *J*(PSe) 743 Hz), 27.8 (s, 1P, *J*(PSe) 737 Hz).

*4.4. Synthesis of $[\{Au(C_6F_5)\}_2(\mu\text{-L1})]$ (**1**)*

To a solution of **L1** (0.081 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Au(C_6F_5)(tht)]$ (0.090 g, 0.2 mmol) and the mixture was stirred for 30 min. Evaporation of the solvent to ca. 5 mL and addition of hexane (10 mL) gave complex **1** as an orange solid. Yield 65%, 100.1 mg. Λ_M 14 Ω^{-1} cm^2 mol^{-1}. $C_{51}H_{37}Au_2F_{10}FeNOP_2Se_2$ (1540.92): calcd. C 39.78, H 2.42, N 0.91; found C 39.54, H 2.47, N 0.93. ^1H NMR, δ: 3.30 (m, 4H, CH_2), 3.75 (m, 4H, CH_2), 4.14 (s + m, 5 + 2H, $C_5H_5 + C_5H_4$), 4.59 (m, 2H, C_5H_4), 7.52–7.83 (m, 20H, Ph). $^{31}P\{^1H\}$, −55 °C, δ: 30.6 (s, 1P, *J*(PSe) 552 Hz), 26.8 (s, 1P, *J*(PSe) 551 Hz). ^{19}F, δ: −116.5 (m, 4F, *o*-F), −160.0 (m, 2F, *p*-F), −162.5 (m, 4F, *m*-F).

*4.5. Synthesis of $[\{Au(C_6F_5)_3\}_2(\mu\text{-L1})]$ (**2**)*

To a solution of **L1** (0.081 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Au(C_6F_5)_3(tht)]$ (0.154 g, 0.2 mmol) and the mixture was stirred for 30 min. Evaporation of the solvent to ca. 5 mL and addition of hexane (10 mL) gave complex **2** as an orange solid. Yield 76%, 167.4 mg. Λ_M 3.8 Ω^{-1} cm^2 mol^{-1}. $C_{75}H_{37}Au_2F_{30}FeNOP_2Se_2$ (2207.70): calcd. C 40.80, H 1.69, N 0.63; found C 40.56, H 1.67, N 0.74. ^1H NMR, δ: 3.20 (m, 8H, CH_2), 4.13 (m, 2H, C_5H_4), 4.17 (m, 2H, C_5H_4), 4.20 (m, 5H, C_5H_5), 7.43–7.76 (m, 20H, Ph). $^{31}P\{^1H\}$, δ: 27.5 (s, 2P); −55 °C, δ: 28.1 (s, 1P), 25.9 (s, 1P). ^{19}F, δ: −120.0 (m, 4F, *o*-F), −121.8 (m, 2F, *o*-F), −122.6 (m, 6F, *o*-F), −156.9 (m, 2F, *p*-F), 156.9 (m, 2F, *p*-F), −157.3 (t, 1P, *p*-F, *J*(FF) 19 Hz), −159.1 (t, 1P, *p*-F, *J*(FF) 19 Hz), −160.0 (t, 1P, *p*-F, *J*(FF) 21 Hz), −160.9 (m, 4F, *m*-F), −161.5 (m, 2F, *m*-F), −162.8 (m, 2F, *m*-F), −163.1 (m, 4F, *m*-F).

Table 1
X-ray data for compounds **L1** and **1**.

Compound	**L1**	**1**
Formula	$C_{39.5}H_{37}ClFeNOP_2Se_2$	$C_{54}H_{43}Au_2Cl_3F_{10}FeNOP_2Se_2$
M_r	852.86	1687.89
Habit	Orange prism	Orange prism
Crystal size (mm)	0.16 × 0.10 × 0.10	0.22 × 0.20 × 0.16
Crystal system	Monoclinic	Triclinic
Space group	*C2/c*	*P-1*
Cell constants		
a (Å)	12.5906(13)	13.7406(8)
b (Å)	23.321(3)	15.1267(9)
c (Å)	25.603(3)	15.2415(9)
α (°)	90	66.9560(10)
β (°)	101.167(3)	71.9100(10)
γ (°)	90	79.9360(10)
V (Å^3)	7375.4(14)	2765.9(3)
Z	8	2
D_x (Mg m^{-3})	1.536	2.027
μ (mm^{-1})	2.575	7.143
$F(000)$	3440	1610
T (°C)	−173	−173
$2\theta_{max}$	50	51
No. of refl.		
Measured	19,815	15,725
Independent	6480	10,139
Transmissions	0.6834–0.7828	0.3025–0.3945
R_{int}	0.112	0.028
Parameters	464	685
Restraints	490	0
wR (F^2, alle refl.)	0.165	0.075
R (I, $>2\sigma(I)$)	0.053	0.036
S	0.761	0.855
Max. $\Delta\rho$ (e Å^{-3})	1.05	1.03

*4.6. Synthesis of $[M(L1)_2]X$ (M = Cu, X = PF_6 (**3**); Ag, X = OTf (**4**))*

To a solution of **L1** (0.081 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Cu(NCMe)_4]PF_6$ (0.018 g, 0.05 mmol) or AgOTf (0.013 g, 0.05 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of diethyl ether (10 mL) gave complexes **3**, or **4** as orange solids. Complex **3**: Yield 80%, 147 mg. Λ_M 107.7 Ω^{-1} cm^2 mol^{-1}. $C_{78}H_{74}CuF_6Fe_2N_2O_2P_5Se_4$ (1831.37): calcd. C 51.15, H 4.07, N 1.53; found C 51.03, H 4.19, N 1.65, S. ^1H NMR, δ: 2.88 (m, 8H, CH_2), 3.44 (m, 8H, CH_2), 5.08 (m, 18H, $C_5H_4 + C_5H_5$), 7.1–7.9 (m, 40H, Ph). ^1H, −55 °C, δ: 3.08 (m, 16H, CH_2), 3.89 (m, 18H, $C_5H_4 + C_5H_5$), 7.1–7.9 (m, 40H, Ph). $^{31}P\{^1H\}$, δ: 29.0 (s, 4P, *J*(PSe) 655 Hz); −55 °C, δ: 32.7 (s, 1P), 28.8 (s, 2P), 32.7 (s, 1P). Complex **4**: Yield 77%, 142 mg. Λ_M 99.8 Ω^{-1} cm^2 mol^{-1}. $C_{79}H_{74}AgF_3Fe_2N_2O_2P_4SSe_4$ (1831.80): calcd. C 51.80, H 4.07, N 1.53, S 1.75; found C 51.43, H 4.11, N 1.61; S 1.71. ^1H NMR, r.t. and −55 °C, δ: 3.0–4.8 (m, 34H, $C_5H_4 + C_5H_5 + CH_2$), 7.2–7.8 (m, 40H, Ph). $^{31}P\{^1H\}$, δ: 55 °C, r.t. and −55 °C, δ: 31.7 (s, 4P, *J*(PSe) 653 Hz).

*4.7. Synthesis of $[PdCl_2(L1)_2]$ (**5**)*

To a solution of **L1** (0.081 g, 0.1 mmol) in dichloromethane (20 mL) was added *trans*-$[PdCl_2(NCPh)_2]$ (0.038 g, 0.1 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to ca. 5 mL and addition of diethyl ether (10 mL) gave complex **5** as a red solid. Yield 72%, 72.3 mg. Λ_M 2.6 Ω^{-1} cm^2 mol^{-1}. $C_{39}H_{37}Cl_2FeNOP_2PdSe_2$ (988.76): calcd. C 47.37, H 3.77, N 1.42; found C 47.26, H 3.65, N 1.44. ^{1}H NMR, δ: 3.61 (m, 4H, CH_2), 4.15 (m, 2H, C_5H_4), 4.24 (m, 2H, C_5H_4), 4.54 (m, 5H, C_5H_5), 4.69 (m, 4H, CH_2), 7.2–8.0 (m, 20H, Ph). $^{31}P\{^1H\}$, δ: 27.5 (s, 2P); −55 °C, δ: 28.1 (s, 1P), 25.9 (s, 1P).

4.8. *Crystallography*

4.8.1. *Crystal structure determinations*

Data were registered on a Bruker SMART APEX CCD. Data collection type: ω-scans. Absorption corrections were based on multiple scans with the program SADABS [23]. The structures were refined on F^2 using the program SHELXL-97 [24]. All non-hydrogen atoms were refined anisotropically. Further crystallographic data is collected in Table 1.

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Appendix A. Supplementary material

CCDC 925249 (**L1**) and 925250 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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