Group 11 Complexes with the Bidentate $(SePPh_2)_2CH_2$ and Tridentate $[(SePPh_2)_2CH]^-$ Ligands

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

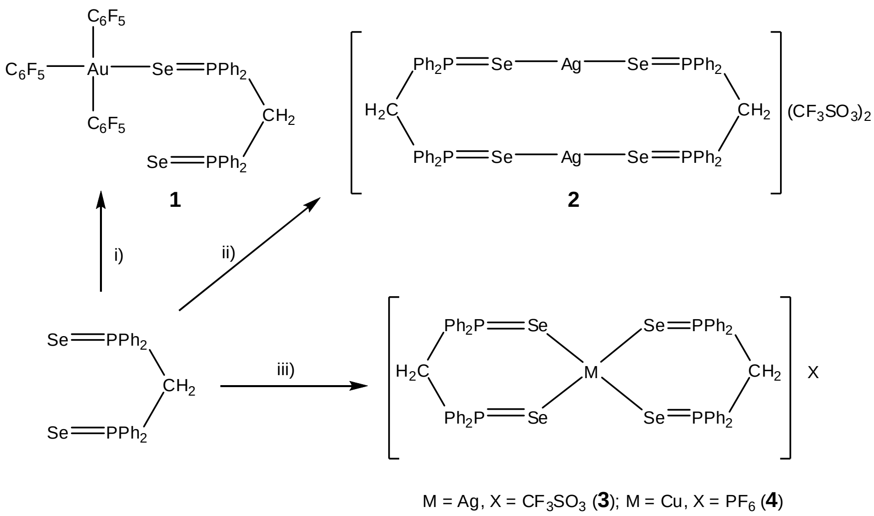
The reaction of $(SePPh_2)_2CH_2$ with group 11 metal complexes such as $[Au(C_6F_5)_3(tht)]$ (tht = tetrahydrothiophene) affords the complex $[Au(C_6F_5)_3(SePPh_2CH_2PPh_2Se)]$ in which the ligand coordinates to the gold(III) center only through one selenium atom. The treatment of the ligand with Ag(OTf) or $[Cu(NCMe)_4]PF_6$ leads, depending on the molar ratio, to the complexes $[Ag_2\{(SePPh_2)_2CH_2\}_2](OTf)_2$ or $[M\{(SePPh_2)_2CH_2\}_2]X$ (M = Ag, X = OTf; M = Cu, X = PF_6; OTf = CF_3SO_3) in which the phosphine selenide ligand coordinates as a bidentate bridging or chelating ligand through the Se,Se atoms. The reaction of $(SePPh_2)_2CH_2$ with $[Au(C_6F_5)_2(acac)]$ (acac = acetylacetonate) occurs with deprotonation of the methylene group, and the methanide complex, $[Au(C_6F_5)_2(SePPh_2CHPPh_2Se)]$, is obtained, with a bidentate chelate Se,C coordination to the gold(III) center. The selenium atom can react further with other metal complexes such as $[Au(C_6F_5)_3(tht)]$ to give the dinuclear species $[Au(C_6F_5)_2\{SePPh_2CHPPh_2SeAu(C_6F_5)_3\}]$, in which the ligand coordinates in a tridentate Se,C,Se form. The crystal structure of $[Au(C_6F_5)_2\{SePPh_2CHPPh_2SeAu(C_6F_5)_3\}]$ has been established by X-ray diffraction.

Key words: Group 11 Metals, Selenium Ligands, Methanide Ligands

Introduction

Gold and the other metals in group 11 have a remarkably affinity for chalcogen elements. However, complexes with sulfur ligands have been much more thoroughly investigated than the corresponding selenium and tellurium derivatives, among which the selenide and selenolate derivatives have been the most studied [1]. Phosphine selenide ligands have been known for a long time but their chemistry has not been widely explored [2, 3]. In particular, few complexes have been described in the chemistry of group 11 metals with this type of ligands. The most studied ligands are the diselenoiminodiphosphinate $[Ph_2P(Se)NP(Se)Ph_2]^-$ or the protonated species, bis(diphenylselenophosphoranyl) amine $[Ph_2P(Se)NHP(Se)Ph_2]$, for which several copper(I) [4, 5] silver(I) [6, 7] and gold(I) and gold(III) [6, 8, 9] complexes have been described. Other complexes reported include the ligands SedppfSe or Sedppf (dppf = 1,1′-bis(diphenylphosphino)ferrocene) [10, 11], $SePR_3$ [12 – 16] or $SePPh_2CH_2PPh_2$ [17 – 19]. The ligand $(SePPh_2)_2CH_2$ has been very rarely used in coordination chemistry [20, 21] including group 11 metal chemistry, and to date only the copper complex $[CuBr(SedppmSe)]_n$ [22] has been structurally characterized. For the deprotonated ligand $[(SePPh_2)_2CH]^-$ only the rhodium derivative $[RhCp\{(SePPh_2)_2CH\}]ClO_4$ has thus been characterized, and no group 11 compound has been prepared [23].

Here we report on the synthesis of several group 11 complexes with the ligands $(SePPh_2)_2CH_2$ and $[(SePPh_2)_2CH]^-$, in which the coordination to the metal centers occurs *via* monodentate Se, bidentate bridging or chelating Se,Se or the tridentate Se,C,Se modes. The latter coordination mode has been structurally characterized in the complex $[Au(C_6F_5)_2\{SePPh_2CHPPh_2SeAu(C_6F_5)_3\}]$.



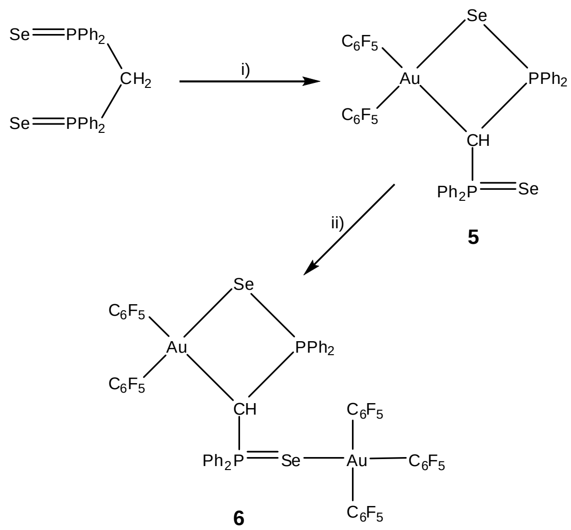
Scheme 1. *i)* $[Au(C_6F_5)_3(tht)]$; *ii)* Ag(OTf); *iii)* 1/2 Ag(OTf) or $[Cu(NCMe)_4]PF_6$.

Results and Discussion

The bis(diphenylselenophosphoryl)methane ligand is easily obtained from the reaction of elemental selenium with bis(diphenylphosphino)methane. In principle, this ligand can coordinate metal centers only through the selenium donor atoms in a monodentate Se or bidentate Se,Se mode but, after deprotonation of the methylene group, it can also coordinate through the methanide carbon atom as a tridentate Se,C,Se donor ligand. We have prepared various group 11 complexes with this ligand in several coordination modes. Thus, the reaction of $(SePPh_2)CH_2$ with $[Au(C_6F_5)_3(tht)]$ leads to the complex $[Au(C_6F_5)_3(SePPh_2CH_2PPh_2Se)]$ (**1**) (see Scheme 1), in which the ligand is monodentate, with coordination through one Se atom. The IR spectrum of **1** shows the absorptions of the pentafluorophenyl groups bonded to a gold(III) center at 1505 (s), 996 (s), 805 (s) and 795 (s) cm^{-1} and the vibration ν(P=Se) at 565 cm^{-1}. The ^1H NMR spectrum shows the protons of the methylene group as a *pseudo* triplet, which indicates that the coupling with the phosphorus atoms is different, and multiplets for the phenyl protons. The $^{31}P\{^1H\}$ NMR spectrum shows an AB system, which proves that the coordination of the ligand takes places through only one of the selenium atoms. In the ^{19}F NMR spectrum six resonances appear for the $Au(C_6F_5)_3$ unit, which corresponds to two types of pentafluorophenyl moieties (ratio 2 : 1); each type presents two multiplets for the *meta* and *ortho* fluorine and a triplet for the *para* fluorine atoms.

The treatment of $(SePPh_2)CH_2$ with Ag(OTf) in a 1 : 1 molar ratio gives the species $[Ag_2\{(SePPh_2)_2CH_2\}_2](OTf)_2$ (**2**). We assume a dinuclear structure with the ligand bridging both silver atoms, rather than a mononuclear structure with a chelating ligand, because the IR spectrum shows the typical absorptions for ionic (non-coordinated) triflate; for a chelated structure, the trifluoromethanesulfonate anion would probably coordinate to the metal center. The $^{31}P\{^1H\}$ NMR spectrum shows only one singlet for the equivalent phosphorus atoms coupled to the selenium nuclei (J(PSe) = 615 Hz). In the ^1H spectrum multiplets for the methylene and the phenyl protons appear. In the mass spectrum (LSIMS+) the peak at m/z = 615 (100 %) appears, which corresponds to the fragment $[Ag\{(SePPh_2)_2\text{-}CH_2\}]^+$.

The reactions of $(SePPh_2)CH_2$ with Ag(OTf) or $[Cu(NCMe)_4]PF_6$ in a 2 : 1 molar ratio give the complexes $[M\{(SePPh_2)_2CH_2\}_2]X$ [M = Ag, X = OTf (**3**); M = Cu, X = PF_6 (**4**)], in which the geometry at the metal centers is probably tetrahedral. The IR spectra of these complexes show the absorptions of counterions OTf^- or $PF_6{}^-$ (846 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectra in each case show one singlet for the phosphorus atoms, also with coupling to the selenium atoms. In the ^1H NMR spectra the methylene protons appear as triplets by coupling to both phosphorus atoms. In the mass spectra the molecular cation at m/z = 1193 (10 %) is observed for complex **3**, whereas for compound **4** only the fragment $[Cu\{(SePPh_2)CH_2\}]^+$ at m/z = 606 (55 %) is detected.



Scheme 2. *i)* [Au(C_6F_5)$_2$(acac)]; *ii)* [Au(C_6F_5)$_3$(tht)].

In order to obtain complexes with the ligand coordinated additionally through the carbon atom, we have carried out the reaction of the ligand with [Au(C_6F_5)$_2$(acac)], in which the acetylacetonate ligand deprotonates the methylene group, forming acetylacetone and the methanide compound [Au(C_6F_5)$_2$(SePPh$_2$CHPPh$_2$Se)] (**5**) (see Scheme 2). Compound **5** is a yellow air- and moisture-stable solid. The IR spectrum shows the absorptions arising from pentafluorophenyl rings in a *cis* disposition and the vibration ν(P=Se). The ^{31}P{^{1}H} NMR spectrum shows the presence of two inequivalent phosphorus atoms at 56.1 and 33.5 ppm, suggesting that one of the selenium atoms is coordinated to the gold(III) center. In the ^{1}H NMR spectrum the methanide proton appears as a *pseudo* triplet. In the ^{19}F NMR spectrum, not only the two pentafluorophenyl rings but in fact all the fluorine atoms are inequivalent, probably owing to hindered rotation of the pentafluorophenyl moieties. In the mass spectrum (LSIMS+) the molecular ion [M]$^+$ with *m/z* = 1075 (20 %) and the fragment [M–C_6F_5]$^+$ (30 %) appear.

Although the structure of compound **5** has not been confirmed by X-ray diffraction, the NMR data indicate a coordination of one selenium and the methanide carbon atoms to the gold(III) center. This coordination is confirmed by reaction of **5** with [Au(C_6F_5)$_3$(tht)], whereby the coordination of this gold fragment to the uncoordinated selenium atom gives the complex [Au(C_6F_5)$_2${SePPh$_2$CHPPh$_2$SeAu(C_6F_5)$_3$}] (**6**). The NMR data indicate two inequivalent phosphorus atoms, the methanide proton appears as a doublet of doublets, and all the pentafluorophenyl rings are inequivalent, including the mutually *trans* rings of the Au(C_6F_5)$_3$ unit, probably because of hindered rotation about the Au–Se bond.

Table 1. Selected bond lengths (Å) and angles (deg) for complex **6**.

Au(1)–C(51)	2.048(3)	Au(2)–C(81)	2.077(3)
Au(1)–C(61)	2.054(3)	Au(2)–Se(2)	2.4940(4)
Au(1)–C(1)	2.153(3)	Se(2)–P(2)	2.1814(8)
Au(1)–Se(1)	2.4639(4)	Se(1)–P(1)	2.1716(10)
Au(1)···P(1)	2.9364(9)	P(2)–C(1)	1.808(3)
Au(2)–C(71)	2.048(3)	P(1)–C(1)	1.813(3)
Au(2)–C(91)	2.061(3)		
C(51)–Au(1)–C(61)	86.76(12)	C(71)–Au(2)–Se(2)	175.43(9)
C(51)–Au(1)–C(1)	97.57(12)	C(91)–Au(2)–Se(2)	93.81(8)
C(61)–Au(1)–C(1)	175.28(12)	C(81)–Au(2)–Se(2)	87.54(9)
C(51)–Au(1)–Se(1)	174.77(10)	P(2)–Se(2)–Au(2)	107.53(3)
C(61)–Au(1)–Se(1)	93.83(8)	P(1)–Se(1)–Au(1)	78.33(3)
C(1)–Au(1)–Se(1)	81.69(8)	P(2)–C(1)–P(1)	120.86(18)
C(71)–Au(2)–C(91)	90.76(12)	P(2)–C(1)–Au(1)	117.93(16)
C(71)–Au(2)–C(81)	87.93(12)	P(1)–C(1)–Au(1)	95.16(14)
C(91)–Au(2)–C(81)	173.75(12)		

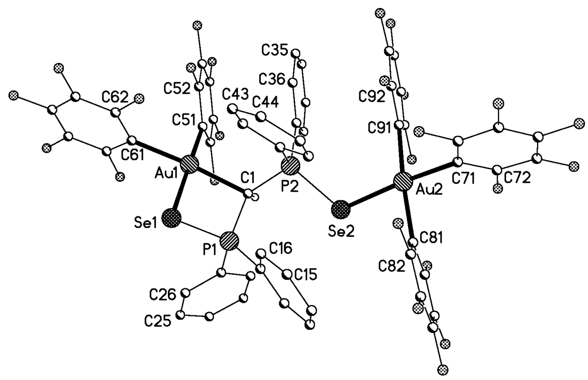


Fig. 1. Molecular structure of complex **6** in the crystal showing the atom labelling scheme (atoms with arbitrary radii; hydrogen atoms omitted for clarity with the exception of the methanide C–H).

The crystal structure of complex **6** has been established by X-ray diffraction and the molecule is shown in Fig. 1. A selection of bond lengths and angles are collected in Table 1. The two gold(III) centers are coordinated to the ligand in a different manner, one being chelated (Se,C for Au1) and the other monodentate (Se at Au2). Both gold centers are in a square planar geometry (r.m.s. deviations of gold and four donor atoms 0.04, 0.06 Å); the (C_6F_5)$_3$Au–Se unit is more regular with angles ranging from 87.54(9) – 93.81(8)° but the other has a narrow bite angle of the chelating ligand, 81.69(8)°. The distances

Au1–Se1 2.4639(4) and Au2–Se2 2.4940(4) Å are significantly different, more so than those found in the only other structurally characterized complex with Au(III)–Se–P bonds, $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$ (2.4808(3) and 2.4832(3) Å) [10]. The Au–C bond lengths to the pentafluorophenyl units are very similar and lie in the range 2.048(3) – 2.077(3) Å; the longest are found for the mutually *trans* pentafluorophenyl units and the shortest *trans* to selenium. The Au1–C1 distance of 2.153(3) Å is longer than the bonds to the pentafluorophenyl rings, but similar to those found in methanide complexes such as $[Au(C_6F_5)_3\{SPPh_2CH(AuC_6F_5)PPh_2CHCOOMe\}]$ (2.119(21) Å) [24]. The folding angle of the four-membered ring about the Se···C axis is 27.1(2)° and the Au···P distance across the ring is 2.9364(9) Å. The Au–C–P–Se–Au backbone displays an extended conformation, with torsion angles 177.7(1)° and −169.4(1)° about C1—P2 and P2—Se2, respectively. The rings at C51, C31 and C91 thereby attain an intramolecular stacking geometry, with interplanar angles C5*x*/C3*x* 3°, C9*x*/C3*x* 6°, intercentroid distances C5*x*/C3*x* 3.51 Å, C9*x*/C3*x* 3.48 Å, and ring offsets C5*x*/C3*x* 0.8 Å, C9*x*/C3*x* 0.9 Å.

Conclusions

In this work, the hitherto poorly explored coordination chemistry of the ligand bis(diphenylselenophosphoryl)methane towards group 11 metal complexes has been investigated. The first examples of complexes with silver(I) and gold(III) are described. Furthermore several complexes of group 11 metals have been synthesized with the ligand in various coordination modes, monodentate to gold(III) through the selenium atom in $[Au(C_6F_5)_3(SePPh_2CH_2PPh_2Se)]$, bidentate Se,Se bridging or chelating in the silver(I) or copper(I) derivatives, and the unprecedented coordination modes bidentately chelating Se,C or tridentate Se,C,Se in the gold(III) derivatives $[Au(C_6F_5)_2(SePPh_2CHPPh_2Se)]$ and $[Au(C_6F_5)_2\{SePPh_2CHPPh_2SeAu(C_6F_5)_3\}]$.

Experimental Section

General procedure

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} M 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 spectrometry (LSIMS) technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer or a Bruker ARX 300 spectrometer in CD_2Cl_2. Chemical shifts are cited relative to $SiMe_4$ (^1H, external), 85 % H_3PO_4 (^{31}P, external), or $CFCl_3$ (^{19}F, external). The starting materials $(SePPh_2)_2CH_2$ [25], $[Au(C_6F_5)_3(tht)]$ [26], $[Cu(NCMe)_4]PF_6$ [27] and $[Au(C_6F_5)_2(acac)]$ [28] were prepared by published procedures.

Preparations

*Bis(diphenylselenophosphoryl)methane-tris(pentafluorophenyl)gold(III) (**1**)*

To a solution of $(SePPh_2)_2CH_2$ (0.054 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Au(C_6F_5)_3(tht)]$ (0.078 g, 0.1 mmol) and the mixture was stirred for 30 min. Evaporation of the solvent to a volume of *ca.* 5 mL and addition of hexane gave complex **1** as a white solid. Yield: 0.078 g (65 %). – Λ_M = 3.5 Ω^{-1} cm^2 mol^{-1}. – $C_{43}H_{22}AuF_{15}P_2Se_2$ (1240.445): calcd. C 41.63, H 1.78; found C 41.74, H 1.78. – ^1H NMR: δ = 4.63 (t, 2H, $^2J(PH)$ = 13 Hz, CH_2), 7.17 – 8.02 (m, 20H, Ph). – $^{31}P\{^1H\}$ NMR: δ = 24.5 (AB system, P_A), 28.8 (AB system, P_B, $^2J(AB)$ = 17 Hz). – ^{19}F NMR: δ = −120.2 (m, 4F, *o*-F), −123.0 (m, 2F, *o*-F), −157.0 (t, *J*(FF) = 19 Hz, 1F, *p*-F), −157.4 (t, *J*(FF) = 19 Hz, 2F, *p*-F), −161.0 (m, 4F, *m*-F), −161.5 (m, 2F, *m*-F).

*Bis[bis(diphenylselenophosphoryl)methane-silver(I) (trifluoromethanesulfonate)] (**2**)*

To a solution of $(SePPh_2)_2CH_2$ (0.054 g, 0.1 mmol) in dichloromethane (20 mL) was added Ag(OTf) (0.026 g, 0.1 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to a volume of *ca.* 5 mL and addition of diethyl ether gave complex **2** as a white solid. Yield: 0.099 g (63 %). – Λ_M = 138 Ω^{-1} cm^2 mol^{-1}. – $C_{52}H_{44}Ag_2F_6O_6P_4S_2Se_4$ (1598.496): calcd. C 39.07, H 2.77, S 4.01; found C 38.69, H 2.50, S 4.02. – ^1H NMR: δ = 4.83 (m, 4H, CH_2), 7.25 – 7.63 (m, 40H, Ph). – $^{31}P\{^1H\}$ NMR: δ = 24.7 (s, *J*(PSe) = 615 Hz, 4P).

*Bis[bis(diphenylselenophosphoryl)methane]silver(I) trifluoromethanesulfonate (**3**)*

To a solution of $(SePPh_2)_2CH_2$ (0.054 g, 0.1 mmol) in dichloromethane (20 mL) was added Ag(OTf) (0.013 g, 0.05 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to leave a volume of *ca.* 5 mL and addition of diethyl ether gave complex **3** as a white solid. Yield: 0.099 g (72 %). – Λ_M = 110 Ω^{-1} cm^2 mol^{-1}. – $C_{51}H_{44}AgF_3O_3P_4SSe_4$ (1341.557): calcd. C 45.66, H 3.30, S 2.39; found C 45.39, H 3.05, S 2.14. – ^1H NMR: δ = 4.56

(t, ^2J(PH) = 13 Hz, 4H, CH_2), 7.26 – 7.77 (m, 40H, Ph). – $^{31}P\{^1H\}$ NMR: δ = 26.2 (s, J(PSe) = 615 Hz, 4P).

*Bis[bis(diphenylselenophosphoryl)methane]copper(I) hexafluorophosphate (**4**)*

To a solution of $(SePPh_2)_2CH_2$ (0.054 g, 0.1 mmol) in tetrahydrofuran (20 mL) was added $[Cu(NCMe)_4]PF_6$ (0.018 g, 0.05 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to leave a volume of *ca.* 5 mL and addition of diethyl ether gave complex **4** as a white solid. Yield: 0.097 g (75 %). – Λ_M = 92 Ω^{-1} cm^2 mol^{-1}. – $C_{50}H_{44}CuF_6P_5Se_4$ (1293.129): calcd. C 46.44, H 3.43; found C 46.15, H 3.40. – ^1H NMR: δ = 4.15 (t, ^2J(PH) = 13 Hz, 4H, CH_2), 7.28 – 7.78 (m, 40H, Ph). – $^{31}P\{^1H\}$ NMR: δ = 21.8 (s, J(PSe) = 673 Hz, 4P).

*[Bis(diphenylselenophosphoryl)methanido]bis(pentafluorophenyl)gold(III) (**5**)*

To a solution of $(SePPh_2)_2CH_2$ (0.054 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Au(C_6F_5)_2(acac)]$ (0.063 g, 0.1 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to leave a volume of *ca.* 5 mL and addition of hexane gave complex **5** as a white solid. Yield: 0.078 g (60 %). – Λ_M = 2.1 Ω^{-1} cm^2 mol^{-1}. – $C_{37}H_{21}AuF_{10}P_2Se_2$ (1072.380): calcd. C 41.44, H 1.97; found C 41.63, H 2.16. – ^1H NMR: δ = 3.77 ("t", ^2J(PH) = 11.3 Hz, 1H, CH), 7.0 – 8.3 (m, 20H, Ph). – $^{31}P\{^1H\}$ NMR: δ = 35.1 (s, 1P, PPh_2Se), 56.1 (s, 1P, $AuSePPh_2$). – ^{19}F NMR: δ = −120.5 (m, 1F, *o*-F), −123.5 (m, 1F *o*-F), −124.4 (m, 1F, *o*-F), −125.3 (m, 1F, *o*-F), −158.6 (t, J(FF) = 19 Hz, 1F, *p*-F), −159.1 (t, J(FF) = 19 Hz, 1F, *p*-F), −161.9 (m, 2F, *m*-F), −161.7 (m, 2F, *m*-F).

*{[Se-Tris(pentafluorophenyl)gold(III)]-C,N-bis(diphenylselenophosphoryl)methanido-bis(pentafluorophenyl)-gold(III)}(**6**)*

To a solution of $[Au(C_6F_5)_2(SePPh_2CHPPh_2Se)]$ (0.107 g, 0.1 mmol) in dichloromethane (20 mL) was added $[Au(C_6F_5)_3(tht)]$ (0.078 g, 0.1 mmol) and the mixture was stirred for 1 h. Evaporation of the solvent to leave a volume of *ca.* 5 mL and addition of hexane gave complex **6** as a white solid. Yield: 0.120 g (68 %). – Λ_M = 3.2 Ω^{-1} cm^2 mol^{-1}. – $C_{55}H_{21}Au_2F_{25}P_2Se_2$ (1770.515): calcd. C 37.31, H 1.19; found C 37.43, H 1.41. – ^1H NMR: δ = 3.60 (dd, ^2J(PH) = 15 and 10 Hz, 1H, CH), 7.0 – 8.1 (m, 20H, Ph). – $^{31}P\{^1H\}$ NMR: δ = 34.1 (d, ^2J(PP) = 13 Hz, J(PSe) = 566 Hz, 1P, PPh_2Se), 34.1 (d, ^2J(PP) = 13 Hz, J(PSe) = 428 Hz, 1P, PPh_2Se). – ^{19}F NMR: δ = −119.4 (m, 2F, *o*-F), −120.2 (m, 2F *o*-F), −120.7 (m, 1F, *o*-F), −121.4 (m, 2F, *o*-F), −122.8 (m, 2F, *o*-F), −123.4 (m, 1F, *o*-F), −124.4 (m, 1F, *o*-F), −156.4 (t, J(FF) = 19 Hz, 2F, *p*-F), −156.7 (t, J(FF) = 20 Hz, 1F, *p*-F), −157.8 (t, J(FF) = 19 Hz, 1F, *p*-F), −157.9 (t, J(FF) = 23 Hz, 3F, *p*-F), −159.8 (m, 1F, *m*-F), −161.0 (m, 4F, *m*-F), −161.5 (m, 1F, *m*-F), −161.8 (m, 4F, *m*-F).

X-Ray structure determination

A suitable single crystal of **6** (0.40 × 0.20 × 0.14 mm^3) was mounted in inert oil on a glass fibre. Data were measured using MoK_α radiation (λ = 0.71073 Å) on a Bruker SMART 1000 CCD diffractometer. *Crystal data:* $C_{55}H_{21}Au_2F_{25}P_2Se_2$, M = 1770.51, monoclinic, space group $P2_1/n$, a = 16.5513(16), b = 18.7736(18), c = 17.9090(18) Å, β = 100.160(3)°, V = 5477.6(9) Å^3, Z = 4, T = −130 °C, D_c = 2.147 Mg m^{-3}, μ = 6.862 mm^{-1}, $F(000)$ = 3328, 117460 reflections measured ($2\theta_{max}$ 60.08°, ω scans), 16036 unique (R_{int} = 0.0570), absorption corrections based on multiple scans (SADABS [29]). The structure was solved by heavy-atom methods, and subjected to full-matrix least-squares refinement on F^2 (SHELXL-97 [30]). All non-hydrogen atoms were refined anisotropically. H atoms were included using a riding model, except for the methanide hydrogen at C1, which was refined freely. Refinement proceeded to $wR(F^2)$ 0.0557, conventional $R(F)$ 0.0260 for 779 parameters and 132 restraints (to local ring symmetry), $S(F^2)$ = 0.951, maximum $\Delta\rho$ = 1.557 e Å^{-3}.

CCDC 629514 contains 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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