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Coordination Behaviour of Gold and Silver Towards Pyrazole Ligands

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Treatment of pyrazole ligands HL (HL = pyrazole or 3,5-dimethylpyrazole) with the gold(I) compound [Au(C_6F_5)(tht)] (tht = tetrahydrothiophene) gives either the complexes [Au(C_6F_5)(HL)] or, if the reaction is carried out in a molar ratio of 1:2 and in the presence of a base, the pyrazolate compound [NBu_4][{Au(C_6F_5)}$_2$(μ-L)]. Binuclear derivatives with bridging pyrazolate ligands have been obtained by treatment of the ligands with [O(AuPPh$_3$)$_3$][ClO_4] or [Au_2Cl_2(μ-dppf)] (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene) and Na_2CO_3, to give [(AuPPh$_3$)$_2$(μ-L)][ClO_4] or [Au_2(μ-L)(μ-dppf)]Cl. Treatment of [Ag(OTf)(PPh$_3$)] with the pyrazole ligands affords the dimeric species [Ag$_2$(μ-OTf)$_2$(HL)$_2$(PPh$_3$)$_2$]. Gold(III) derivatives have been accessed by treatment of the pyrazole ligands with [Au(C_6F_5)$_3$(OEt_2)] or [Au(C_6F_5)$_2$(OEt_2)$_2$][ClO_4], affording the species [Au(C_6F_5)$_3$(HL)] or [Au(C_6F_5)$_2$(HL)$_2$][ClO_4]. Gold(III) pyrazolate derivatives of the form *trans*-[NBu_4][Au(C_6F_5)$_2$Cl(L)] or [{Au(C_6F_5)$_2$}$_2$(μ-L)$_2$] have been prepared from [NBu_4][Au(C_6F_5)$_2$Cl$_2$] or [Au(acac)(C_6F_5)$_2$]. X-ray structural characterization has been carried out for eight compounds.

Introduction

The chemistry of pyrazole and pyrazolate metal complexes is quite extensive, as shown by the notable reviews by Trofimenko[1,2] and La Monica et al.[3] Although pyrazole and pyrazolate complexes with gold have been less intensively studied than those of other metals, many gold(I) derivatives have been reported; they include cyclic trinuclear complexes, [Au_3L_3] or [$Au_xAg_{3-x}L_3$] (L = varied pyrazolate ligands), some of them showing interesting properties such as luminescence or liquid crystal properties,[4–13] gold(I) derivatives with high nuclearity,[14–17] or binuclear and mononuclear pyrazole or pyrazolate gold(I) complexes.[18–26] In contrast with gold(I), only a few examples of pyrazole or pyrazolate derivatives of gold(III) have been synthesized; these include cyclic trinuclear compounds of the types Au^I_2/Au^{III}, Au^I/Au^{III}_2 or Au^{III}_3, prepared by oxidation of the corresponding trinuclear gold(I) pyrazolates, and binuclear or mononuclear derivatives of the types [$AuCl_2$(μ-L)]$_2$, [$AuCl_3$(HL)] or [$AuCl_2$(L)(HL)].[18,27–30] In addition to the properties of these kinds of complexes mentioned above, the biological activities of some derivatives have been studied with promising results.[21,30]

The chemistry of silver(I) pyrazolate complexes is also quite extensive and, as in the case of related gold(I) compounds, cyclic trinuclear derivatives are an important class of coordination compounds with significant properties.[5,10,11,31–35] In addition, several binuclear and mononuclear pyrazole and pyrazolate silver(I) complexes are also known.[24,36–38]

In this work we present the synthesis of gold(I), gold(III) and silver(I) complexes with the ligands Hpz (pyrazole) and Hpz′ (3,5-dimethylpyrazole). We have synthesized mononuclear derivatives with the pyrazole as ligand or binuclear species with the pyrazolate acting as bridging ligand. The gold(III) complexes represent some of the few examples of this type of complexes. Exhaustive structural characterization of the gold(I) and gold(III) compounds has been carried out by X-ray diffraction. Furthermore, these derivatives are good candidates for biological screening. Pyrazole itself has been shown to be cytotoxic, and gold and silver complexes display antitumor and antimicrobial activities.[21,30]

Results and Discussion

Synthesis of the Complexes

Synthesis of Gold(I) and Silver(I) Complexes

Treatment of equimolecular amounts of Hpz or Hpz′ with [Au(C_6F_5)(tht)] (tht = tetrahydrothiophene) affords the complexes [Au(C_6F_5)(HL)] [L = pz (**1**) or pz′ (**2**)] as air- and moisture-stable, white solids (see Scheme 1). Their IR spectra show absorptions from the pentafluorophenyl group at 1505 (s), 949 (s) and 807 (s) cm^{-1} for complex **1** and 1504 (s), 952 (s) and 803 (s) cm^{-1} for complex **2**.

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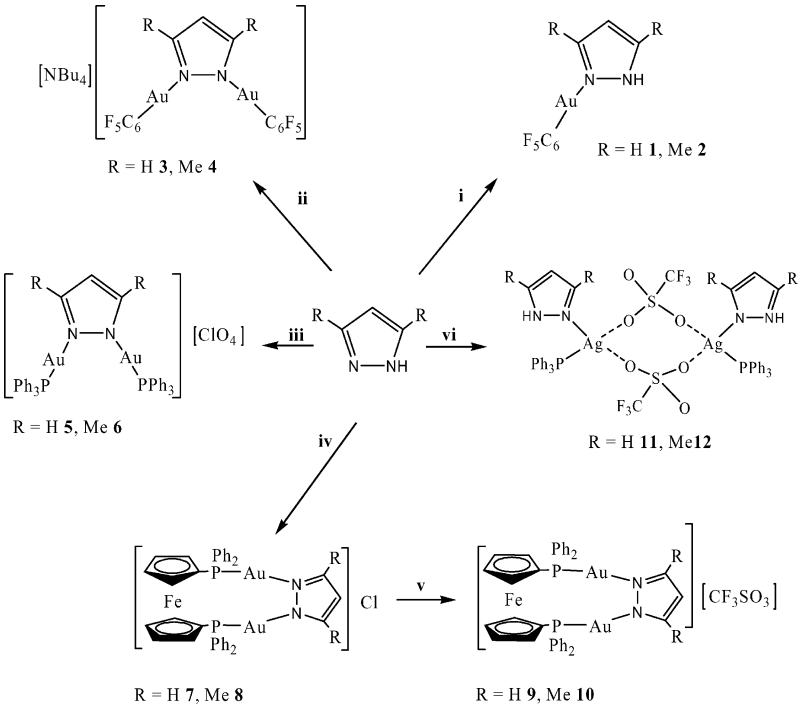


Scheme 1. **i** = $[Au(C_6F_5)(tht)]$, **ii** = $2[Au(C_6F_5)(tht)] + (NBu_4)(acac)$, **iii** = $[O(AuPPh_3)_3][ClO_4]$, **iv** = $[Au_2Cl_2(\mu\text{-dppf})] + Na_2CO_3(s)$, **v** = [AgOTf], **vi** = $[Ag(OTf)(PPh_3)]$.

The ^1H NMR spectra of **1** and **2** show the resonances for the pyrazole ligands: four multiplets [4-H, 3-H, 5-H and 2-H(NH)] for **1** and four singlets [$2 \times CH_3$, 4-H and 2-H(NH)] for **2**. The ^{19}F NMR spectra of the two compounds each present two multiplets for the *ortho* and *meta* and a triplet for the *para* fluorine. In the liquid secondary-ion mass spectra (LSIMS) the molecular peaks appear at *m*/*z* = 432 (46%, **1**) and 460 (61%, **2**).

Treatment of $[Au(C_6F_5)(tht)]$ with $(NBu_4)(acac)$ and Hpz or Hpz′ in a molar ratio of 2:1:1 gave the binuclear complexes $[NBu_4][\{Au(C_6F_5)\}_2(\mu\text{-L})]$ [L = pz (**3**), pz′ (**4**)] as white, air- and moisture-stable solids. In the IR spectra, absorptions at ca. 1500 (s), 956 (s) and 800 (s) cm^{-1} from the pentafluorophenyl groups are observed.

The ^1H NMR spectra show (apart from the multiplets from the cation protons) one triplet for 4-H and one doublet for the equivalent protons 3-H and 5-H in the case of complex **3**, and in that of complex **4** two singlets, one of them corresponding to the equivalent protons of the CH_3 groups and the other to 4-H. The ^{19}F NMR spectra of both compounds each present two multiplets for the *ortho* and *meta* and a triplet for the *para* fluorine. In the $LSIMS^-$ spectra of these derivatives the peaks assigned to the fragments $[M - NBu_4]^-$ appear at *m*/*z* = 795 (100%, **3**) and 824 (100%, **4**).

Treatment of the free ligands Hpz and Hpz′ with $[O(AuPPh_3)_3][ClO_4]$ in 1:1 molar ratio gave the binuclear derivatives $[(AuPPh_3)_2(\mu\text{-L})]ClO_4$ [L = pz (**5**) or pz′ (**6**)] as white solids that are air- and moisture-stable at room temperature. In the IR spectra the absorptions arising from anionic perchlorate appear at 1094 (vs, br.) and 623 (s) cm^{-1}. The ^1H NMR spectra show the resonances for the pyrazolate ligand and the phenyl rings in the appropriate ratio. The $^{31}P\{^1H\}$ NMR spectrum of each compound is one singlet because of the equivalence of the phosphorus atoms. In the $LSIMS^+$ mass spectra the cationic molecular peaks appear at *m*/*z* (%) = 985 (100, for **5**) and 1013 (100, for **6**).

Treatment of equimolecular amounts of Hpz and Hpz′ with $[Au_2Cl_2(\mu\text{-dppf})]$ [dppf = 1,1′-bis(diphenylphosphanyl)-ferrocene] in the presence of Na_2CO_3 afforded yellow solids: the complexes $[Au_2(\mu\text{-L})(\mu\text{-dppf})]Cl$ [L = pz (**7**), pz′ (**8**)]. They are air- and moisture-stable. Attempts to obtain the complexes containing two pyrazolate ligands failed, in spite of the various approaches that were tested. Treatment of **7** and **8** with [AgOTf] in a molar ratio of 1:1 led to the complexes **9** and **10** as yellow solids. The solid IR spectra of **9** and **10** each present bands at 1270 (vs, br), 1223 (s), 1154 (s) and 1030 (s) cm^{-1}, arising from the trifluoromethanesulfonate.

The ^1H NMR spectra of **7**, **8**, **9** and **10** each show two multiplets for the α and β protons of the cyclopentadienyl groups, together with the resonances for pyrazolate ligands and the phenyl rings in the appropriate ratio. The $^{31}P\{^1H\}$ NMR spectrum of each one shows a singlet because of the equivalence of the phosphorus atoms. In the $LSIMS^+$ mass spectra the cationic molecular peaks appear at *m*/*z* (%) = 1015 (100, **7**, **9**) and 1043 (100, **8**, **10**).

The crystal structures of the dinuclear complexes **3**, **6** and **10** have been established by X-ray diffraction studies and are shown in Figures 1, 2 and 3, respectively. Selected bond lengths and angles are collected in Table 1. The geometry around the gold atoms is linear but slightly distorted:

N–Au–C angles in **3** are 174.48(13)° and 176.11(13)°, whereas N–Au–P angles in **6** and **10** range from 174.63(3)° to 178.55(9)°. The Au···Au distances in complexes **6** and **10** – 3.3238(2) and 3.2776(3) Å – indicate weak aurophilic interactions, while the Au···Au distance of 3.499 Å in **3** may be long enough to preclude a significant degree of metal–metal bonding.

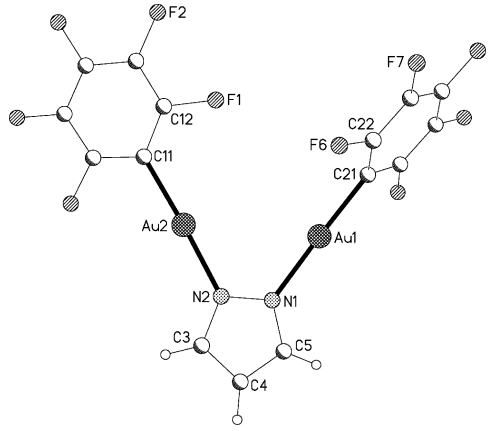


Figure 1. Structure of the anion of complex **3** showing the atom labelling scheme; radii are arbitrary.

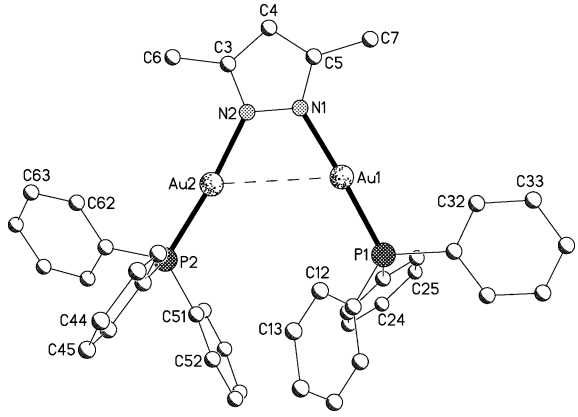


Figure 2. Structure of the cation of the complex **6** with the atom labelling scheme; H atoms are omitted for clarity.

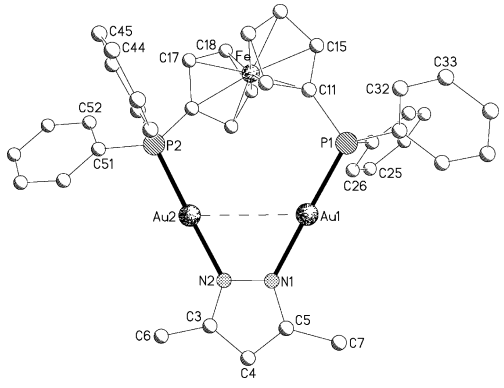


Figure 3. Structure of the cation of the complex **10** with the atom labelling scheme; H atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **3**, **6** and **10**.

Compound **3**			
Au(1)–C(21)	2.002(3)	Au(2)–C(11)	2.008(4)
Au(1)–N(1)	2.034(3)	Au(2)–N(2)	2.035(3)
C(21)–Au(1)–N(1)	174.48(13)	C(11)–Au(2)–N(2)	176.12(13)
Compound **6**			
Au(1)–N(1)	2.0394(17)	Au(2)–N(2)	2.0437(18)
Au(1)–P(1)	2.2369(6)	Au(2)–P(2)	2.2444(6)
Au(1)–Au(2)	3.32381(18)		
N(1)–Au(1)–P(1)	176.76(5)	N(2)–Au(2)–P(2)	174.63(5)
N(1)–Au(1)–Au(2)	62.00(5)	N(2)–Au(2)–Au(1)	60.77(5)
P(1)–Au(1)–Au(2)	115.076(15)	P(2)–Au(2)–Au(1)	124.290(15)
Compound **10**			
Au(1)–N(1)	2.037(3)	Au(2)–N(2)	2.028(3)
Au(1)–P(1)	2.2365(9)	Au(2)–P(2)	2.2358(9)
Au(1)–Au(2)	3.2776(3)		
N(1)–Au(1)–P(1)	176.05(11)	N(2)–Au(2)–P(2)	178.55(9)
N(1)–Au(1)–Au(2)	62.12(9)	N(2)–Au(2)–Au(1)	61.85(9)
P(1)–Au(1)–Au(2)	118.13(2)	P(2)–Au(2)–Au(1)	116.84(3)

The Au–N [2.034(3) and 2.035(3) Å] and Au–C [2.002(3) and 2.008(4) Å] bond lengths in complex **3** are of the same order as those found in other complexes containing the N–Au–C_6F_5 moiety, such as [Au(C_6F_5)(FcCH_2NHpyMe)] [2.073(4) and 1.988(4) Å],[39] [Au(C_6F_5)(3-Fcpy)] [2.124(15) and 2.00(2) Å][40] or [Au(C_6F_5)(Ph_2C=N–N=CPh_2)] [2.069(5) and 1.992(6) Å].[41]

The Au–N and Au–P bond lengths for complexes **6** and **10** compare well with those found in the related compounds [Au_2(μ-3,5-Ph_2pz)(PPh_3)$_2$][NO_3] or [Au_2(μ-3,5-Ph_2pz)(μ-dppp)][NO_3] [dppp = bis(diphenylphosphanyl)propane],[25] in which pyrazolate also acts as a bidentate ligand, or with those found in other pyrazole or pyrazolate-gold(I) complexes containing the N–Au–P core.[14,19–23]

Complexes **3** and **6** each show several C–H···F and C–H···O interactions that might be interpreted as hydrogen bonds (Table 2).

Table 2. Hydrogen bonds for compounds **3** and **6** [Å and °].

Compound **3**[a] D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
C(3)–H(3)···F(2)#1	0.95	2.56	3.223(5)	127.5
C(43)–H(43B)···F(6)	0.99	2.57	3.522(4)	161.6
C(32)–H(32B)···F(9)#2	0.99	2.56	3.467(4)	153.0
C(45)–H(45B)···F(8)#2	0.99	2.39	3.134(5)	131.6
C(37)–H(37A)···F(5)#3	0.99	2.59	3.328(4)	131.2
C(45)–H(45A)···F(7)#1	0.99	2.59	3.473(4)	148.6
Compound **6**[b] D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
C(15)–H(15)···O(1)#1	0.95	2.50	3.441(3)	171.0
C(24)–H(24)···O(3)#2	0.95	2.57	3.189(3)	123.4
C(55)–H(55)···O(4)#2	0.95	2.53	3.428(3)	158.7

[a] Symmetry transformations used to generate equivalent atoms: #1: *x*, *y* + 1, *z*; #2: –*x* + 1, –*y* + 1, –*z* + 2; #3: –*x* + 1, –*y* + 2, –*z* + 1. [b] Symmetry transformations used to generate equivalent atoms: #1: –*x* + 3/2, *y* – 1/2, –*z* + 1/2; #2: *x* – 1/2, –*y* + 3/2, *z* + 1/2.

Treatment of the free ligands Hpz and Hpz′ with [Ag(OTf)(PPh$_3$)] (1:1 molar ratio) led to the complexes [Ag(HL)(PPh$_3$)][OTf] [L = pz (**11**) or pz′ (**12**)] (Scheme 1) as air- and moisture-stable, white solids. The IR spectra of complexes **11** and **12** each present absorptions at ca 1275, 1255, 1224, 1160 and 1030 cm^{-1} arising from the triflate group. The ^{1}H NMR spectrum of **11** shows three multiplets, one for the 2-H(NH), one for the 4-H and one for the protons 3-H and 5-H; the resonances for complex **12** are two singlets for the 4-H and 2-H(NH) and one multiplet for the CH_3 protons. The LSIMS$^+$ spectra show the cation molecular peaks at *m*/*z* = 437 (30%, **11**) and 465 (30%, **12**).

The structures of compounds **11** and **12** have also been established by X-ray diffraction methods (Figures 4 and 5, respectively). Selected bond lengths and angles are shown in Table 3. Each complex has a dimeric structure with the triflate groups acting as bridging ligands. The silver atoms display highly distorted tetrahedral geometries: the angles around Ag range from 82.83(4)° to 155.31(4)° in the case of **11** and from 74.24(8)° to 159.73(9)° in that of **12**. The long Ag–O bonds [2.6331(12), 2.7343(13) Å for **11** and 2.6565(27), 2.7295(31) Å for **12**] are consistent with the weak bonds often found in silver-triflate complexes.

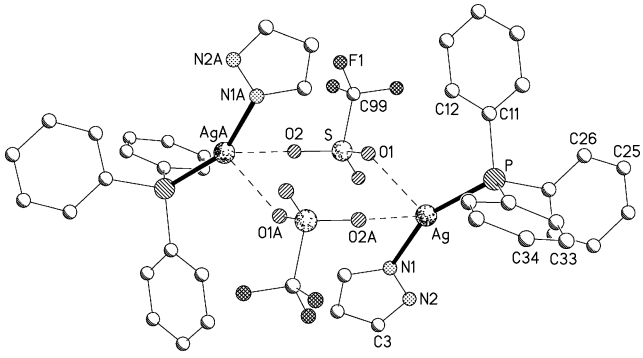


Figure 4. Molecular structure of complex **11**; radii are arbitrary. H atoms are omitted for clarity.

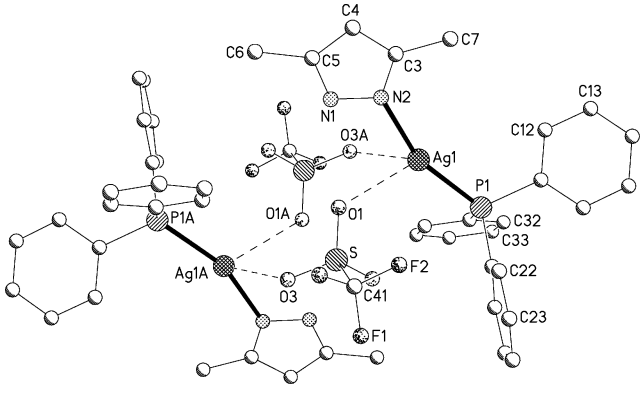


Figure 5. Molecular structure of complex **12**; radii are arbitrary. H atoms are omitted for clarity.

The Ag–N bond lengths – 2.1791(13) Å (complex **11**) and 2.178(3) Å (complex **12**) – compare well with that observed in the tetracoordinate silver compound [Ag(OTf)(pzCH$_2$Fc)(PPh$_3$)] [2.196(4) Å],[42] which has the same type of dinuclear structure, but are shorter than those found in other four-coordinate pyrazole-silver complexes such as [Ag$_2$(pz)$_2$(PPh$_3$)$_3$] [2.295(2) and 2.323(2) Å for the tetracoordinate silver atom],[36] [Ag{HB(Pz)$_3$}(PPh$_3$)] [from 2.325(4) to 2.355(3) Å][43] or in other tetrahedral silver complexes containing bis(pyrazolyl)alkane ligands as reported in references 44 and 45 [ranging from 2.234(2) to 2.5092(19) Å].[44,45] The Ag–P bond lengths [2.3645(4) (complex **11**) and 2.3598(13) Å (complex **12**)] compare well with those observed in complexes [Ag(OTf)(pzCH$_2$Fc)(PPh$_3$)][42] and [Ag{HB(Pz)$_3$}(PPh$_3$)][43] but are slightly shorter than those found in [Ag$_2$(pz)$_2$(PPh$_3$)$_3$].[36]

Additionally, complexes **11** and **12** each show several hydrogen bonds, listed in Table 4.

Table 3. Selected bond lengths [Å] and angles [°] for compounds **11** and **12**.

Compound **11**[a]			
Ag–N(1)	2.1791(13)	Ag–O(1)	2.6331(12)
Ag–P	2.3645(4)	Ag–O(2)#1	2.7343(13)
N(1)–Ag–P	155.31(4)	N(1)–Ag–O(2)#1	92.23(5)
N(1)–Ag–O(1)	88.48(5)	P–Ag–O(2)#1	103.21(3)
P–Ag–O(1)	112.23(3)	O(1)–Ag–O(2)#1	82.83(4)
Compound **12**[b]			
Ag(1)–N(2)	2.178(3)	Ag(1)–O(3)_#1	2.6565 (27)
Ag(1)–P(1)	2.3598(13)	Ag(1)–O(1)	2.7295 (31)
N(2)–Ag(1)–P(1)	159.73(9)	O(1)–Ag(1)–O(3)_#1	74.24(8)
N(2)–Ag(1)–O(1)	79.20(10)	P(1)–Ag(1)–O(1)	117.77(6)
N(2)–Ag(1)–O(3)_#1	83.43(10)	P(1)–Ag(1)–O(3)_#1	110.88 (7)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x, -y + 1, -z + 1$. [b] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y + 1, -z$.

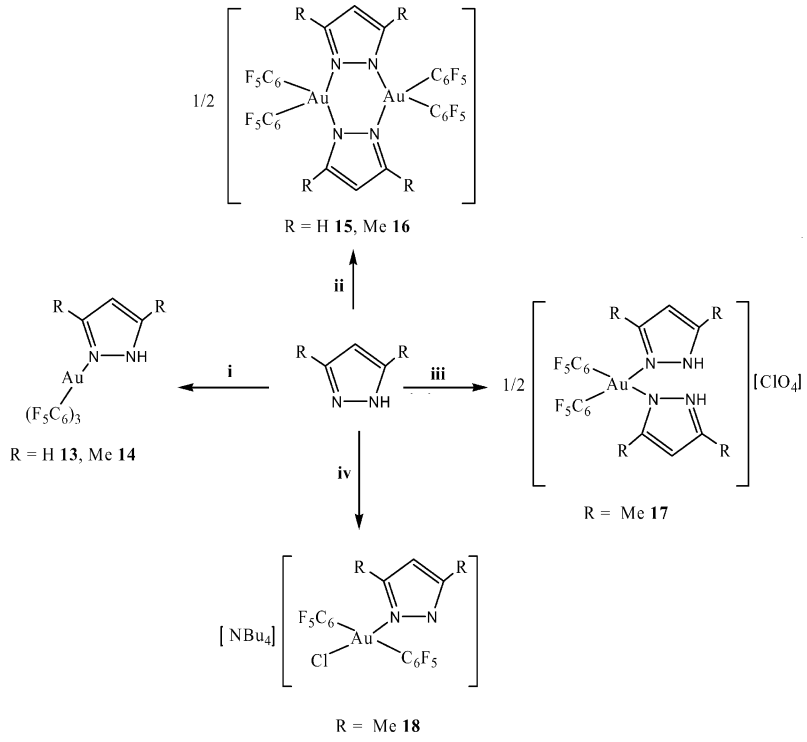
Table 4. Hydrogen bonds for compounds **11** and **12** [Å and °].

Compound **11**[a]				
D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(2)–H(2)···O(3)#2	1.05(3)	2.00(3)	3.019(2)	163(2)
C(5)–H(5)···O(1)#1	0.95	2.41	3.316(3)	159.5
(12)–H(12)···O(1)	0.95	2.40	3.330(2)	166.0
C(36)–H(36)···O(2)#1	0.95	2.56	3.356(2)	142.0
Compound **12**[b]				
D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(1)–H(1)···O(1)	0.86	2.40	2.907(4)	118.3
N(1)–H(1)···O(2)#1	0.86	2.36	3.111(4)	146.7

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x, -y + 1, -z + 1$; #2: $-x + 1, -y + 1, -z + 1$. [b] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y + 1, -z$.

Gold(III) Complexes

Treatment of Hpz or HPz′ with [Au(C$_6$F$_5$)$_3$(OEt$_2$)] led to the mononuclear gold(III) complexes [Au(C$_6$F$_5$)$_3$(Hpz)] (**13**) or [Au(C$_6$F$_5$)$_3$(Hpz′)] (**14**) as white, air- and moisture-stable solids (see Scheme 2). In the IR spectra of complexes **13** and **14**, strong absorptions at ca. 1510, 965, 819 and 795 cm^{-1}, from the pentafluorophenyl groups, are observed.



Scheme 2.**i** = $[Au(C_6F_5)_3(OEt_2)]$, **ii** = $[Au(acac)(C_6F_5)_2]$, **iii** = $1/2[Au(C_6F_5)_2(OEt_2)_2][ClO_4]$, **iv** = $[NBu_4][Au(C_6F_5)_2Cl_2] + Na_2CO_3(s)$.

The ^1H NMR spectra show three multiplets (4-H, 3-H and 5-H) and a broad signal [2-H(NH)] for **13** and four singlets [$2 \times CH_3$, 4-H and 2-H(NH)] for **14**. The ^{19}F NMR spectrum of each compound presents six resonances corresponding to two types of pentafluorophenyl groups in a 2:1 ratio, for the *ortho*, *meta* and *para* fluorines of each (C_6F_5) unit. In the liquid secondary-ion mass spectra the molecular peaks appear at *m*/*z* = 766 (**13**, 10%) and 794 (**14**, 10%).

We also prepared the binuclear neutral gold(III) complexes $[\{Au(C_6F_5)_2\}_2(\mu\text{-}L)_2]$ [L = pz (**15**), pz′ (**16**)], in which the pyrazolates act as bridging ligands between the two gold(III) centres, starting from $[Au(acac)(C_6F_5)_2]$ and Hpz or Hpz′. They are air- and moisture-stable, white solids. In the solid state, the *cis* configurations of each pair of C_6F_5 groups are confirmed[46,47] by the presence of two IR bands at 819 and 810 cm^{-1} for **15** and at 815 and 804 cm^{-1} for **16**.

The pyrazolate ligands are equivalent in solution, as reflected by the ^1H NMR spectra: in the case of **15** one doublet (3-H and 5-H) and one triplet (4-H) appear, whereas in that of **16** two singlets in a 6:1 ratio appear for the methyl protons and the 4-H. The ^{19}F NMR spectrum of **15** shows two different *ortho* and *meta* fluorines (in a 1:1 ratio) but only one *para* fluorine; the latter observation indicates that the two $Au(C_6F_5)_2$ units are equivalent, and the former that the pentafluorophenyl rings cannot rotate. In contrast, the ^{19}F NMR spectrum of complex **16** presents only three resonances (*ortho*, *para* and *meta* fluorines); there is no hindered rotation and only one kind of pentafluorophenyl ring is observed. In the LSIMS the molecular peaks do not appear but the fragments M/2 are present at *m*/*z* = 599 (10%) for complex **15** and at 627 (10%) for complex **16**.

Treatment of Hpz′ with $[Au(C_6F_5)_2(OEt_2)_2][ClO_4]$, prepared in situ, in a 2:1 ratio led to the mononuclear gold(III) complex $[Au(C_6F_5)_2(Hpz')_2][ClO_4]$ (**17**, Scheme 2) as a white, air- and moisture-stable solid. Its IR spectrum shows two bands characteristic of the ClO_4 anion at 1082 (s, br) and 620 (s) cm^{-1}, along with two others in the 800 cm^{-1} region [811 (s) and 799 (s) cm^{-1}], which confirm the *cis* configuration of the C_6F_5 groups.[46,47] The four singlets observed in the ^1H NMR spectrum indicate the equivalence of the pyrazole ligands, whereas the three resonances observed in the ^{19}F NMR spectrum indicate that there is no hindered rotation of the pentafluorophenyl groups. The $LSIMS^+$ spectrum shows the cation molecular peak at *m*/*z* = 723 (100%).

Treatment of equimolecular amounts of Hpz′ with $[NBu_4][Au(C_6F_5)_2Cl_2]$ in the presence of Na_2CO_3 afforded the complex *trans*-$[NBu_4][Au(C_6F_5)_2Cl(pz')]$ (**18**) as a yellow solid that is air- and moisture-stable. Attempts to prepare the complex containing two pz′ units were unsuccessful. The IR spectrum presents bands at 1506 (s), 961 (s) and 791 (s) cm^{-1}, arising from the pentafluorophenyl groups, and at 352 (s) cm^{-1}, due to the ν(Au–Cl) vibration.

The ^1H NMR spectrum shows, apart from the multiplets for the cation protons, three singlets, two of them corresponding to the non-equivalent protons of the CH_3 and the other to the 4-H. The ^{19}F NMR spectrum presents two multiplets for the *ortho* and *meta* and a triplet for the *para* fluorine. The $LSIMS^-$ spectrum shows the anion molecular peak at *m*/*z* = 662 (100%).

The structures of complexes **15**, **17** and **18** have been determined by X-ray diffraction studies (Figures 6, 7 and 8,

respectively). The gold atoms in these complexes each show the expected square-planar geometry: mean deviations of the planes formed by the four donor atoms and the gold centre are 0.035 [Au(1)] and 0.043 Å [Au(2)] (compound **15**), 0.006 (compound **17**) and 0.017 Å (compound **18**). The dinuclear complex **15** adopts the typical boat conformation that is also observed in the related complex $[Au_2Cl_4(\mu\text{-}pz)_2]$,[30] and the short intramolecular gold(III)···gold(III) distance of 3.435 Å is probably imposed by the doubly bridging pyrazolate ligands. Selected bond lengths and angles for complexes **15**, **17** and **18** are collected in Table 5.

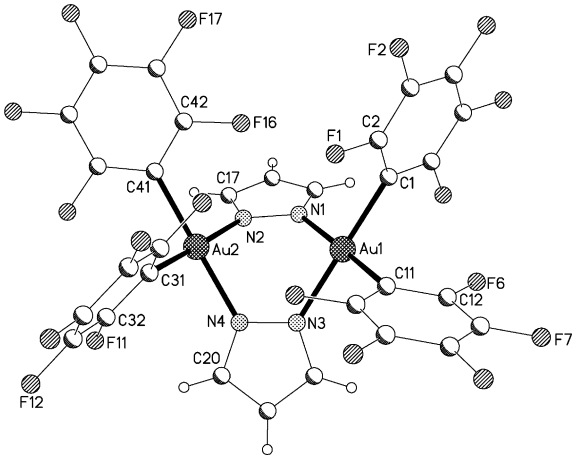


Figure 6. Molecular structure of complex **15** showing the atom labelling scheme; radii are arbitrary.

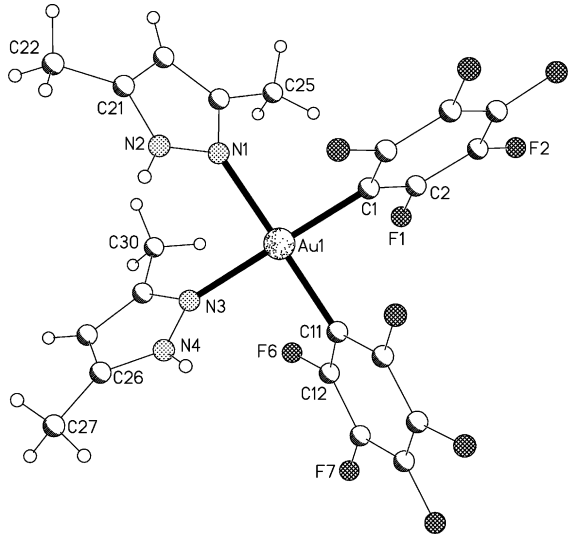


Figure 7. Structure of the cation of complex **17** showing the atom labelling scheme; radii are arbitrary.

The Au–N [ranging from 2.049(4) to 2.075(9) Å] and Au–C [ranging from 2.010(5) to 2.019(6) Å] bond lengths in **15** and **17** compare well with those observed in the complex $[Au(C_6F_5)_2(3\text{-}Fcpy)_2][ClO_4]$ [Au–N, 2.076(7) and 2.089(7); Au–C 2.011(9) and 2.015(9) Å][40] and are shorter than those found in the complexes $[AuMe_2(tpzm)][NO_3]$ (tpzm = tri-1-pyrazolylmethane) [Au–N, 2.129(5) and 2.141(5) Å; Au–C, 2.023(7) and 2.031(8) Å][48] or $[AuMe_2\{B(pz)_4\}]$ [$B(pz)_4$ = tetrakis(pyrazol-1-yl)borate] [Au–N, 2.096(6) and 2.101(8) Å; Au–C, 2.03(1) and 2.04(2) Å].[49]

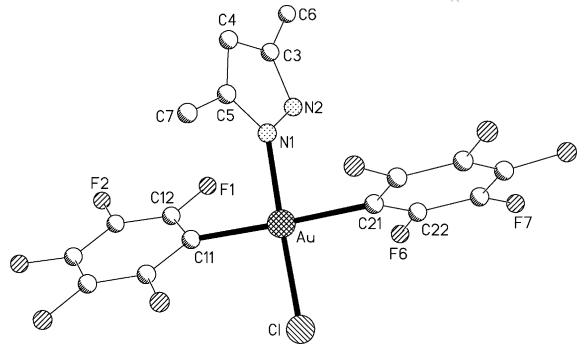


Figure 8. Structure of the anion of complex **18** showing the atom labelling scheme; radii are arbitrary.

Table 5. Selected bond lengths [Å] and angles [°] for compounds **15**, **17** and **18**.

Compound **15**			
Au(1)–C(11)	2.010(5)	Au(2)–C(41)	2.016(5)
Au(1)–C(1)	2.019(5)	Au(2)–C(31)	2.017(5)
Au(1)–N(1)	2.049(4)	Au(2)–N(4)	2.054(4)
Au(1)–N(3)	2.053(4)	Au(2)–N(2)	2.062(4)
C(11)–Au(1)–C(1)	87.5(2)	C(41)–Au(2)–C(31)	87.5(2)
C(11)–Au(1)–N(1)	177.69(19)	C(41)–Au(2)–N(4)	179.17(19)
C(1)–Au(1)–N(1)	92.98(19)	C(31)–Au(2)–N(4)	92.80(18)
C(11)–Au(1)–N(3)	89.57(18)	C(41)–Au(2)–N(2)	90.78(19)
C(1)–Au(1)–N(3)	176.6(2)	C(31)–Au(2)–N(2)	175.6(2)
N(1)–Au(1)–N(3)	89.85(17)	N(4)–Au(2)–N(2)	88.86(17)
Compound **17**			
Au(1)–C(1)	2.013(11)	Au(1)–N(3)	2.063(9)
Au(1)–C(11)	2.014(10)	Au(1)–N(1)	2.075(9)
C(1)–Au(1)–C(11)	88.5(4)	C(1)–Au(1)–N(1)	92.1(4)
C(1)–Au(1)–N(3)	178.6(4)	C(11)–Au(1)–N(1)	179.2(4)
C(11)–Au(1)–N(3)	90.9(4)	N(3)–Au(1)–N(1)	88.5(4)
Compound **18**			
Au–N(1)	1.9955(17)	Au–C(11)	2.072(2)
Au–C(21)	2.057(2)	Au–Cl	2.2928(5)
N(1)–Au–C(21)	88.32(7)	N(1)–Au–Cl	178.45(5)
N(1)–Au–C(11)	89.48(7)	C(21)–Au–Cl	90.14(5)
C(21)–Au–C(11)	177.07(8)	C(11)–Au–Cl	92.07(5)

In complex **18** the Au–N distance [1.9957(17) Å] is shorter than in **15** and **17**, consistently with a higher *trans* influence of the pentafluorophenyl ligand than of the chlorine ligand. The Au–C distances [2.0717(22) and 2.0568(23) Å] lie in the same range as Au–C distances to mutually *trans* pentafluorophenyl groups in the complex $[Au(C_6F_5)_3(3\text{-}Fcpy)]$ [2.067(3) and 2.068(3) Å].[40]

Compound **17** displays several short and reasonably linear N–H···O, C–H···O and C–H···F contacts that might be interpreted as hydrogen bonds (Table 6).

Some of these pyrazole/pyrazolate complexes might potentially have been treated with other metallic compounds to provide heteronuclear derivatives. However these reac-

Table 6. Hydrogen bonds for compound **17** [Å and °].[a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(2)–H(2)···O(2)#1	0.88	2.22	3.066(14)	161.8
N(2)–H(2)···O(1)#1	0.88	2.38	3.064(14)	134.8
N(4)–H(4)···O(4)#2	0.88	2.14	2.942(13)	151.9
C(27)–H(27B)···F(6)#3	0.98	2.45	3.367(14)	155.6
C(28)–H(28)···O(3)#4	0.95	2.40	3.268(17)	151.9

[a] Symmetry transformations used to generate equivalent atoms: #1: x, $y + 1$, z; #2: $-x + 1$, $-y + 1$, $-z + 2$; #3: $-x$, $-y + 2$, $-z + 2$; #4: $x - 1$, $y + 1$, z.

tions proved not to be clean, and mixtures of the desired compounds together with homonuclear complexes were obtained.

Conclusions

Several derivatives of gold(I), gold(III) or silver(I) in combination with pyrazole or pyrazolate ligands have been synthesized. The coordination behaviour shown by the ligands depends on whether they are the neutral pyrazole or the anionic pyrazolate ligands. They therefore act in the complexes as monodentate (pyrazoles) or bidentate bridging ligands (pyrazolate). There is only one exception in which a pyrazolate acts a monodentate ligand, uncommon in the coordination behaviour of this type of ligands: in the gold(III) species $NBu_4[Au(C_6F_5)_2Cl(pz')]$. Several complexes have been structurally characterized, providing examples of coordination modes and Au^{I}–N and Au^{III}–N bond lengths, the latter not well represented in the literature. All attempts to obtain heteronuclear complexes by treatment of some of these derivatives with other metal compounds have led to a mixture of complexes in which the desired heteronuclear species were present only together with other homonuclear species.

Experimental Section

Instrumentation: IR spectra were recorded in the 4000–200 cm^{-1} range on a Perkin–Elmer 883 spectrophotometer by use of Nujol mulls between polyethylene sheets. C, H and N analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Austopec, by use of the LSIMS technique, with nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external) and 85% H_3PO_4 (^{31}P, external).

Starting Materials: The starting materials $[Au(C_6F_5)(tht)]$,[50] $[O(AuPPh_3)_3][ClO_4]$,[51] $[Au_2Cl_2(\mu\text{-dppf})]$,[52] $[Ag(OTf)(PPh_3)]$,[53] $[Au(C_6F_5)_3(OEt_2)]$,[54] $[Au(acac)(C_6F_5)_2]$,[55] $[Au(C_6F_5)_2(OEt_2)_2][ClO_4]$,[55] and $[NBu_4][Au(C_6F_5)_2Cl_2]$[56] were prepared by published procedures. All other chemicals used were commercially available and used without further purification.

Caution: Perchlorates with organic cations may be explosive.

Synthesis of $[Au(C_6F_5)(HL)]$ [L = pz (1), pz′ (2)]: Hpz (0.020 g, 0.3 mmol) or Hpz′ (0.029 g, 0.3 mmol) was added to a dichloromethane solution (20 mL) of $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene; 0.136 g, 0.3 mmol). The reaction mixture was stirred for 1 h and concentrated to ca. 5 mL, and addition of hexane (15 mL) led to complexes **1** or **2** as white solids.

Complex 1: Yield 48%, 62.22 mg. ^1H NMR: δ = 6.70 (m, 1 H, pz, 4-H), 7.87 (m), 7.92 (m, 2 H, pz, 3-H, 5-H), 11.19 (br. m, 1 H, pz, 2-H NH) ppm. ^{19}F NMR: δ = –116.84 (m, 2 F, *o*-F), –159.65 (t, $J_{p\text{-}F,m\text{-}F}$ = 19.97 Hz, 1 F, *p*-F), –163.32 (m, 2 F, *m*-F) ppm. $C_9H_4AuF_5N_2$ (432.10): calcd. C 25.02, H 0.93, N 6.48; found C 24.88, H 1.10, N 6.34.

Complex 2: Yield 65%, 89.73 mg. ^1H NMR: δ = 2.37 (s), 2.45 (s, 6 H, pz′, 2 × CH_3), 6.16 (s, 1 H, pz′, 4-H), 10.15 (br. s, 1 H, pz′, 2-H NH) ppm. ^{19}F NMR: δ = –116.66 (m, 2 F, *o*-F), –160.07 (t, $J_{p\text{-}F,m\text{-}F}$ = 19.98 Hz, 1 F, *p*-F), –163.51 (m, 2 F, *m*-F) ppm. $C_{11}H_8AuF_5N_2$ (460.15): calcd. C 28.71, H 1.75, N 6.09; found C 28.56, H 1.43, N 6.16.

Synthesis of $[NBu_4][\{Au(C_6F_5)\}_2(\mu\text{-L})]$ [L = pz (3), pz′ (4)]: (NBu_4)(acac) (0.068 g, 0.2 mmol) and either Hpz (0.014 g, 0.2 mmol) or Hpz′ (0.019 g, 0.2 mmol) were added to a dichloromethane solution (20 mL) of $[Au(C_6F_5)(tht)]$ (0.181 g, 0.4 mmol), and the solution was stirred for 2 h. Partial evaporation of the solvent (5 mL) and addition of diethyl ether (15 mL) led to the precipitation of **3** or **4** as white solids.

Complex 3: Yield 69%, 143.19 mg. ^1H NMR: δ = 0.89 (t, $^3J_{H,H}$ = 7.27 Hz, 12 H, CH_3), 1.29 (m, 8 H, CH_2), 1.50 (m, 8 H, CH_2), 3.07 (m, 8 H, CH_2), 6.50 (t, $^3J_{H,H}$ = 2.23 Hz, 1 H, pz, 4-H), 7.61 (d, $^3J_{H,H}$ = 2.23 Hz, 2H pz, 3-H, 5-H) ppm. ^{19}F NMR: δ = –115.51 (m, 4 F, *o*-F), –161.25 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 21.27 Hz, 2 F, *p*-F), –164.03 (m, 4 F, *m*-F) ppm. $C_{31}H_{39}Au_2F_{10}N_3$ (1037.58): calcd. C 35.88, H 3.78, N 4.04; found C 35.43, H 3.79, N 4.14.

Complex 4: Yield 74%,157.71 mg. ^1H NMR: δ = 0.80 (t, $^3J_{H,H}$ = 7.32 Hz, 12 H, CH_3), 1.16 (m, 8 H, CH_2), 1.39 (m, 8 H, CH_2), 2.25 (s, 6 H, pz′, 2 × CH_3), 2.97 (m, 8 H, CH_2), 6.05 (s, 1 H, pz, 4-H) ppm. ^{19}F NMR: δ = –115.45 (m, 4 F, *o*-F), –161.61 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 21.27 Hz, 2 F, *p*-F), –164.17 (m, 4 F, *m*-F) ppm. $C_{33}H_{43}Au_2F_{10}N_3$ (1065.63): calcd. C 37.19, H 4.06, N 3.94; found C 37.52, H 3.89, N 3.72.

Synthesis of $[\{Au(PPh_3)\}_2(\mu\text{-L})][ClO_4]$ [L = pz (5), pz′(6)]: pz (0.0068 g, 0.1 mmol) or pz′ (0.0096 g, 0.1 mmol) was added to a dichloromethane solution (20 mL) of $[O\{Au(PPh_3)\}_3][ClO_4]$ (0.1493 g, 0.1 mmol). After stirring for 2 h, the solution was concentrated to ca. 5 mL. Then, diethyl ether was added (15 mL) to provide **3** or **4** as white solids.

Complex 5: Yield 85%, 92.22 mg. ^1H NMR: δ = 6.77 (m, 1 H, pz, 4-H), 7.32–7.51 (m, 30 H, Ph), 7.83 (m, 2 H, pz, 3-H and 5-H) ppm. $^{31}P\{^1H\}$ NMR: δ = 31.27 (s, 2 P, PPh_3) ppm. $C_{39}H_{33}Au_2ClN_2O_4P_2$ (1085.02): calcd. C 43.17, H 3.06, N 2.58; found C 43.18, H 3.01, N 2.19.

Complex 6: Yield 90%, 100.18 mg. ^1H NMR: δ = 2.42 (s, 6 H, 2 × CH_3), 6.37 (s, 1 H, pz′), 7.34–7.51 (m, 30 H, Ph) ppm. $^{31}P\{^1H\}$ NMR: δ = 31.96 (s, 2 P, PPh_3) ppm. $C_{41}H_{37}Au_2ClN_2O_4P_2$ (1113.08): calcd. C 44.24, H 3.35, N 2.52; found C 43.95, H 3.56, N 2.21.

Synthesis of $[Au_2(\mu\text{-L})(\mu\text{-dppf})]Cl$ [L = pz (7), pz′ (8)]: $[Au_2Cl_2(\mu\text{-dppf})]$ (0.204 g, 0.2 mmol) and either Hpz (0.014 g, 0.2 mmol) or Hpz′ (0.019 g, 0.2 mmol) were added to a suspension of Na_2CO_3 (0.020 g, 0.2 mmol) in dichloromethane (20 mL), and the mixture was stirred for 3 h. The suspension was filtered to remove the NaCl formed. Concentration of the solution to approximately 5 mL and addition of diethyl ether gave complexes **7** or **8** as yellow solids.

Complex 7: Yield 73%, 153.42 mg. ^1H NMR: δ = 4.25 (m, 4 H, C_5H_4), 4.65 (m, 4 H, C_5H_4), 6.56 (br. m, 1 H, pz, 4-H), 7.55–7.75

(m, 20 H, Ph and 2 H, pz, 3-H, 5-H) ppm. $^{31}P\{^1H\}$ NMR: δ = 26.23 (s, 2 P, dppf) ppm. $C_{37}H_{31}Au_2ClFeN_2P_2$ (1050.83): calcd. C 42.29, H 2.97, N 2.66; found C 41.91, H 3.38, N 2.92.

Complex 8: Yield 71%, 153.20 mg. ^1H NMR: δ = 2.33 (s, 6 H, CH_3), 4.27 (m, 4 H, C_5H_4), 4.60 (m, 4 H, C_5H_4), 6.35 (br. s, 1 H, pz, 4-H), 7.56–7.60 (m, 20 H, Ph) ppm. $^{31}P\{^1H\}$ NMR: δ = 26.90 (s, 2 P, dppf) ppm. $C_{39}H_{35}Au_2ClFeN_2P_2$ (1078.89): calcd. C 43.42, H 3.27, N 2.60; found C 43.15, H 2.94, N 2.41.

[Au$_2$(μ-dppf)(μ-L)][OTf] [L = pz (9), pz′ (10)]: [AgOTf] (0.026 g, 0.1 mmol) was added to a solution of complex **7** (0.105 g, 0.1 mmol) or **8** (0.108 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 1 h. The suspension was filtered to remove the AgCl formed. Partial evaporation of the solvent (5 mL) and addition of diethyl ether (15 mL) led to the precipitation of **9** or **10** as yellow solids.

Complex 9: Yield 64%, 74.52 mg. ^1H NMR: δ = 4.14 (m, 4 H, C_5H_4), 4.65 (m, 4 H, C_5H_4), 6.82 (m, 1 H, pz, 4-H), 7.57–7.61 (m, 20 H, Ph), 7.82 (m, 2 H, pz, 3-H, 5-H) ppm. $^{31}P\{^1H\}$ NMR: δ = 26.08 (s, 2 P, dppf) ppm. $C_{38}H_{31}Au_2F_3FeN_2O_3P_2S$ (1164.45): calcd. C 39.19, H 2.68, N 2.40; found C 39.54, H 2.83, N 2.34.

Complex 10: Yield 80%, 95.4 mg. ^1H NMR: δ = 2.39 (s, 6 H, CH_3), 4.18 (m, 4 H, C_5H_4), 4.64 (m, 4 H, C_5H_4), 6.40 (s, 1 H, pz′, 4-H), 7.47–7.63 (m, 20 H, Ph) ppm. $^{31}P\{^1H\}$ NMR: δ = 26.96 (s, 2 P, dppf) ppm. $C_{40}H_{35}Au_2F_3FeN_2O_3P_2S$ (1192.50): calcd. C 40.29, H 2.96, N 2.35; found C 40.05, H 2.53, N 2.16.

Synthesis of [Ag(HL)(PPh$_3$)][OTf] [L = pz(11), pz′(12)]: Hpz (0.014 g, 0.2 mmol) or Hpz′ (0.019 g, 0.2 mmol) was added to a dichloromethane solution (20 mL) of [Ag(OTf)(PPh$_3$)] (0.104 g, 0.2 mmol), and the mixture was stirred for 2 h. The solution was concentrated to ca. 5 mL, and addition of diethyl ether (15 mL) gave complexes **11** or **12** as white solids.

Complex 11: Yield 60%, 70.48 mg. ^1H NMR: δ = 6.47 (m, 1 H, pz, 4-H), 7.47–7.53 (m, 15 H, Ph), 7.69 (m, 2 H, pz, 3-H and 5-H), 12.97 (m, 1 H, pz, 2-H NH) ppm. $^{31}P\{^1H\}$ NMR (–55 °C): δ = 15.78 (2 × d, $J_{^{107}Ag,P}$ = 669, $J_{^{109}Ag,P}$ = 772 Hz) ppm. $C_{22}H_{19}AgF_3N_2O_3PS$ (587.30): calcd. C 44.99, H 3.26, N 4.77; found C 44.80, H 3.36, N 5.05.

Complex 12: Yield 79%, 97.22 mg. ^1H NMR: δ = 2.28 (m, 6 H, 2 × CH_3), 5.94 (s, 1 H, pz′, 4-H), 7.46–7.51 (m, 15 H, Ph), 12.10 (s, 1 H, pz, 2-H NH) ppm. $^{31}P\{^1H\}$ NMR (–55 °C): δ = 15.38 (2 br. d, $J_{^{107}Ag,P}$ = 623, $J_{^{109}Ag,P}$ = 746 Hz] ppm. $C_{24}H_{23}AgF_3N_2O_3PS$ (615.35): calcd. C 46.84, H 3.77, N 4.55; found C 46.85, H 3.68, N 4.53.

Synthesis of [Au(C$_6$F$_5$)$_3$(HL)] [L = pz (13), pz′ (14)]: Hpz (0.014 g, 0.2 mmol) or Hpz′ (0.019 g, 0.2 mmol) was added to a freshly prepared diethyl ether solution (20 mL) of [Au(C$_6$F$_5$)$_3$(OEt$_2$)] (0.15 g, 0.2 mmol). The mixture was stirred for 1 h, and the solution was then evaporated to ca. 5 mL; addition of hexane (15 mL) gave complexes **13** or **14** as white solids.

Complex 13: Yield 63%, 96.54 mg. ^1H NMR: δ = 6.49 (m, 1 H, pz, 4-H), 7.50 (m), 7.72 (m, pz, 2 H, 3-H, 5-H), 7.99 (br. m, 1 H, pz, 2-H NH) ppm. ^{19}F NMR: δ = –121.89 (m, 2 F, *o*-F), –122.73 (m, 4 F, *o*-F), –155.22 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 20.15 Hz, 2 F, *p*-F), –156.19 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 20.15 Hz, 1 F, *p*-F), –160.09 (m, 4 F, *m*-F), –161.16 (m, 2 F, *m*-F) ppm. $C_{21}H_4AuF_{15}N_2$ (766.21): calcd. C 39.92, H 0.53, N 3.66; found C 39.80, H 0.62, N 3.24.

Complex 14: Yield 68%, 108.02 mg. ^1H NMR: δ = 2.29 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 6.05 (s, 1 H, pz′, 4-H), 10.70 (s, 1 H, pz′, 2-H NH) ppm. ^{19}F NMR: δ = –122.76 (m, 2 F, *o*-F), –124.11 (m, 4 F, *o*-F), –156.38 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 19.64 Hz, 2 F, *p*-F), –156.96 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 21.27 Hz, 1 F, *p*-F), –160.90 (m, 4 F, *m*-F), –161.83 (m, 2 F, *m*-F) ppm. $C_{23}H_8AuF_{15}N_2$ (794.26): calcd. C 34.78, H 1.01, N 3.53; found C 34.74, H 1.19, N 3.08.

Synthesis of [{Au(C$_6$F$_5$)$_2$}$_2$(μ-L)$_2$] [L = pz (15), pz′ (16)]: Hpz (0.014 g, 0.2 mmol) or Hpz′ (0.019 g, 0.2 mmol) was added to a dichloromethane solution (20 mL) of [Au(C$_6$F$_5$)$_2$(acac)] (0.126 g, 0.2 mmol, acac = acetylacetonate), and the mixture was stirred for 3 h. Concentration of the solution to approximately 5 mL and addition of hexane (15 mL) gave complexes **15** or **16** as white solids.

Complex 15: Yield 50%, 59.81 mg. ^1H NMR: δ = 6.45 (t, $^3J_{H,H}$ = 2.44 Hz, 2 H, pz, 4-H), 7.51 (d, $^3J_{H,H}$ = 2.44 Hz, 4 H, pz, 3-H, 5-H) ppm. ^{19}F NMR: δ = –122.25 (m, 4 F, *o*-F), –124.73 (m, 4 F, *o*-F), –153.81 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 19.63 Hz, 4 F, *p*-F), –159.38 (m, 4 F, *m*-F), –160.05 (m, 4 F, *m*-F) ppm. $C_{30}H_6Au_2F_{20}N_4$ (1196.30): calcd. C 30.12, H 0.50, N 4.68; found C 29.99, H 0.65, N 4.74.

Complex 16: Yield 44%, 55.10 mg. ^1H NMR: δ = 2.15 (s, 12 H, CH_3), 5.93 (s, 1 H, pz′, 4-H) ppm. ^{19}F NMR: δ = –119.62 (m, 4 F, *o*-F), –154.61 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 21.31 Hz, 2 F, *p*-F), –160.97 (m, 4 F, *m*-F) ppm. $C_{34}H_{14}Au_2F_{20}N_4$ (1252.40): calcd. C 32.61, H 1.12, N 4.47; found C 32.99, H 1.22, N 4.44.

Synthesis of [Au(C$_6$F$_5$)$_2$(HL)$_2$][ClO$_4$] [L = pz′(17)]: Hpz′ (0.038 g, 0.4 mmol) was added to a freshly prepared solution of [Au(C$_6$F$_5$)$_2$(OEt$_2$)$_2$][ClO$_4$] (0.2 mmol) in diethyl ether, and the mixture was stirred for 2 h. Complex **17** precipitated as a white solid and was filtered off. Yield 40%, 65.82 mg. ^1H NMR: δ = 2.23 (s, 6 H, CH_3), 2.29 (s, 6 H, CH_3), 6.02 (s, 2 H, pz′, 4-H), 12.08 (s, 2 H, 2-H NH) ppm. ^{19}F NMR: δ = –122.82 (m, 4 F, *o*-F), –153.02 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 20.67 Hz, 2 F, *p*-F), –159.42 (m, 4 F, *m*-F) ppm. $C_{22}H_{16}AuClF_{10}N_4O_4$ (822.79): calcd. C 32.11, H 1.96, N 6.81; found C 32.65, H 2.21, N 7.05.

Synthesis of [NBu$_4$][Au(C$_6$F$_5$)$_2$LCl] [L = pz′(18)]: [NBu$_4$][Au(C$_6$F$_5$)$_2$Cl$_2$][NBu$_4$] (0.169 g, 0.2 mmol) and Hpz′ (0.019 g, 0.2 mmol) were added to a suspension of Na_2CO_3 (0.02 g, 0.2 mmol) in dichloromethane (20 mL), and the mixture was stirred for 3 h. The suspension was filtered to remove the NaCl formed. Concentration of the solution to approximately 5 mL and addition of hexane gave complex **18** as a yellow solid. Yield 51%, 92.22 mg. ^1H NMR: δ = 0.98 (t, $^3J_{H,H}$ = 7.20 Hz, 12 H, CH_3), 1.40 (m, 8 H, CH_2), 1.61 (m, 8 H, CH_2), 2.10 (s, 3 H, pz′, CH_3), 2.16 (s, 3 H, pz′, CH_3), 3.11 (m, 8 H, CH_2), 5.66 (s, 1 H, pz′, 4-H) ppm. ^{19}F NMR: δ = –123.76 (m, 4 F, *o*-F), –160.40 (t, $^3J_{p\text{-}F,m\text{-}F}$ = 20.12 Hz, 2 F, *p*-F), –163.04 (m, 4 F, *m*-F) ppm. $C_{33}H_{43}AuClF_{10}N_3$ (904.12): calcd. C 43.84, H 4.64, N 4.64; found C 43.82, H 4.48, N 4.70.

X-ray Crystallography: Data were recorded with a Siemens P4 (for **12**), a Bruker SMART 1000 CCD (for **3**, **6**, **10**, **11**, **18**) or a Bruker SMART Apex CCD (for **15**, **17**) diffractometer. Data collection type: ω- and ϕ-scans (for **3**, **6**, **10**, **11**, **18**), ω-scans (**15**, **17**), or θ–2θ (**12**). Absorption corrections were based on psi-scans (**12**) multi-scans (for **3**, **11**, **15**, **17**, **18**) or face-indexing (for **6**, **10**). The structures were refined by use of the program SHELXL-97.[57] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included either as rigid methyl groups or by use of a riding model (exception: NH of **11** refined freely). Restraints were applied where necessary to light-atom displacement parameters and local ring symmetry. Further details are given in Tables 7 and 8. Refinement special details: The structure of complex **10** contains one dichloromethane molecule that is disordered over three positions. For **18**, the Flack parameter refined to 0.006(2).

CCDC-690568 (for **3**), -690569 (for **6**), -690570 (for **10**), -690571 (for **11**), -690572 (for **12**), -690573 (for **15**), -690574 (for **17**), and -690575 (for **18**) contain the supplementary crystallographic data

Table 7. Details of data collection and structure refinement for complexes **3**, **6**, **10** and **11**.

Compound	**3**	**6**	**10** CH_2Cl_2	**11**
Chemical formula	$C_{31}H_{39}Au_2F_{10}N_3$	$C_{41}H_{37}Au_2ClN_2O_4P_2$	$C_{41}H_{31}Au_2Cl_2F_3FeN_2O_3P_2S$	$C_{22}H_{19}AgF_3N_2O_3PS$
Crystal habit	colourless needle	colourless plate	orange prism	colourless tablet
Crystal size [mm]	$0.40 \times 0.06 \times 0.04$	$0.30 \times 0.18 \times 0.05$	$0.32 \times 0.27 \times 0.13$	$0.22 \times 0.22 \times 0.16$
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a [Å]	8.7470(8)	15.6916(10)	13.6393(12)	9.1177(6)
b [Å]	9.8133(10)	15.1236(10)	23.4380(18)	11.6357(8)
c [Å]	20.410(2)	15.9511(10)	14.9830(12)	12.5979(8)
α [°]	80.192(3)	–	–	87.139(3)
β [°]	80.813(3)	90.705(3)	115.523(3)	69.868(3)
γ [°]	83.805(3)	–	–	69.099(3)
V [Å^3]	1698.3(3)	3785.1(4)	4322.3(6)	1168.24(13)
Z	2	4	4	2 (monomers)
D_c [g cm^{-3}]	2.029	1.953	1.954	1.670
M	1037.58	1113.05	1271.36	587.29
F(000)	988	2136	2424	588
T [°C]	–130	–130	–130	–130
$2\theta_{max}$ [°]	60	60	60	60
μ(Mo-K_α) [mm^{-1}]	8.709	7.943	7.402	1.071
Transmission	0.722–0.128	0.683–0.19	0.417–0.145	0.962–0.775
No. of reflections measured	32344	69836	79814	23701
No. of unique refl.	9906	11061	12627	6798
R(int.)	0.0398	0.0430	0.0516	0.0235
R [$F > 4\sigma(F)$]	0.0259	0.0178	0.0280	0.0242
wR (F^2, all reflections)	0.0514	0.0376	0.0797	0.0655
No. of reflections used	9906	11061	12627	6798
No. of parameters	415	471	536	302
No. of restraints	84	136	461	0
S	0.911	0.959	1.034	1.049
Max. $\Delta\rho$ [e Å^{-3}]	1.266	0.781	1.913	0.749

Table 8. Details of data collection and structure refinement for complexes **12**, **15**, **17** and **18**.

Compound	**12**	**15**	**17**	**18**
Chemical formula	$C_{24}H_{23}AgF_3N_2O_3PS$	$C_{30}H_6Au_2F_{20}N_4$	$C_{22}H_{16}AuClF_{10}N_4O_4$	$C_{33}H_{43}AuClF_{10}N_3$
Crystal habit	colourless tablet	colourless prism	colourless prism	yellow tablet
Crystal size [mm]	$0.60 \times 0.60 \times 0.40$	$0.40 \times 0.32 \times 0.20$	$0.18 \times 0.16 \times 0.08$	$0.39 \times 0.30 \times 0.20$
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	Cc
a [Å]	10.334(2)	18.893(2)	9.1264(17)	14.0666(10)
b [Å]	10.619(2)	8.3789(9)	11.706(2)	16.9638(12)
c [Å]	12.950(3)	21.252(2)	12.762(2)	16.3843(12)
α [°]	68.76(3)	–	93.963(4)	–
β [°]	75.51(3)	112.519(2)	92.973(4)	111.812(3)
γ [°]	88.91(3)	–	98.257(4)	–
V [Å^3]	1278.4(4)	3107.9(6)	1343.5(4)	3629.8(5)
Z	2	4	2	4
D_c [g cm^{-3}]	1.599	2.557	2.034	1.654
M	615.34	1196.32	822.80	904.12
F(000)	620	2208	788	1792
T [°C]	–100	–173	–173	–130
$2\theta_{max}$ [°]	50	54	50	60
μ(Mo-K_α) [mm^{-1}]	0.983	9.583	5.681	4.205
Transmission	0.695–0.590	0.250–0.114	0.659–0.428	0.930–0.656
No. of reflections measured	7364	18588	7371	38566
No. of unique reflections	4391	6716	4666	10522
R(int.)	0.0586	0.0496	0.0754	0.0236
R [$F > 4\sigma(F)$]	0.0385	0.0320	0.0611	0.0153
wR (F^2, all reflections)	0.0910	0.0741	0.1536	0.0364
No. of reflections used	4391	6716	4666	10522
No. of parameters	318	505	383	435
No. of restraints	0	38	0	116
S	1.051	0.978	1.029	1.006
Max. $\Delta\rho$ [e Å^{-3}]	1.098	1.985	1.900	0.826

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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