Synthesis and ligand properties towards gold and silver of the ferrocenylamidobenzimidazole ligand

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Abstract

The treatment of FcCOCl (Fc = $(C_5H_5)Fe(C_5H_4)$) with aminobenzimidazole in 1:1 or 2:1 ratio gives the ferrocenyl-amido derivatives FcCO(benzimNH$_2$) or (FcCO)$_2$(NHbenzim), respectively. The reactivity of FcCO(benzimNH$_2$) with silver or gold complexes has been studied. The reaction with the basic gold compounds [Au(acac)(PPh$_3$)] or [O(AuPPh$_3$)$_3$]ClO$_4$ occurs with deprotonation of the NH$_2$ group and coordination of one or three gold(phosphine) fragments. The treatment of this ligand with silver compounds, such as Ag(OTf) or [Ag(OTf)(PPh$_3$)], gives the complexes of stoichiometry [Ag(OTf)L] or [Ag(OTf)(PPh$_3$)L]. The ligand FcCO(benzimNH$_2$) and the complex [Ag(OTf){FcCO(benzimNH$_2$)}(PPh$_3$)] have been characterized by X-ray diffraction studies. DFT calculations were performed on models of this dimeric silver complex and showed that dimerization is energetically favourable, because Ag(I) achieves a four coordination environment, despite some bonds being relatively weak.
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Keywords: Gold; Silver; Ferrocene derivatives; DFT calculations; Azolate ligands

1. Introduction

Ferrocene is a very versatile molecule with important properties such as high electron density, aromaticity and redox reversibility. These characteristics, together with the ease of preparation of mono substituted ferrocene derivatives with a great variety of organic and inorganic fragments, make ferrocene a versatile building block in many fields of research. Then ferrocene derivatives are important in areas requiring special properties such as non-optical linearity, charge transport, liquid crystallinity, electrochemical recognition, catalysis or nanoparticles [1–12]. Furthermore, the ferrocenium ion has shown some antitumor potential, albeit at rather high concentrations

[13,14]. Recently, the incorporation of ferrocene into diphenols has been shown to enhance the antiproliferative effects in vitro [15]. Additionally, compounds derived of 2-aminobenzimidazole are know to exhibit a great spectra of biological properties [16–20]. Therefore, the combination of both ferrocene and 2-aminobenzimidazole moieties may be interesting for the possible biological properties. Some ferrocenylalkyl benzimidazoles have been described and they present biological activity, namely ferrocenylmethyl benzimidazole and ferrocenylalkyl polyfluorobenzimidazoles, which show antitumor properties [21–23].

Here we report on the synthesis of two ferrocene amido derivatives obtained by reaction of the chlorocarbonyl ferrocene and 2-aminobenzimidazole and also their reactivity towards gold and silver derivatives. Taking into account that many gold complexes show antiarthritic and anticancer properties, together with the well known antibacterial activity of silver compounds, we think that these ligands

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and their complexes can be optimal candidates for a biological screening.

2. Results and discussion

The synthesis of the ferrocenyl-azolate ligands has been carried out by reaction of Fc(COCl) with 2-aminobenzimidazole (NH_2(benzimH)) in dichloromethane and in the presence of NEt_3. When the reaction is carried out in a ratio 1:1 the compound $FcCO$(benzimNH_2) (**1**) is obtained, as a consequence of the reaction of the NH azole group, and further treatment of this derivative with Fc(COCl), or just the reaction in a 2:1 molar ratio, gives the double amide ligand $(FcCO)_2$(NHbenzim) (**2**) (see Scheme 1). These compounds are red solids air and moisture stable. The ligand **1** was characterized by infrared spectroscopy, which showed the strong $v_{C=O}$ stretching at 1678 cm^{-1} and the sharp v_{N-H}(as) signal at 3415 cm^{-1} among other bands assigned to the ferrocenyl subunit [24]. The comparison between the IR spectra of 2-aminobenzimidazole and **1** led to the assignment of the bands at 1650 ($v_{C=N}$), 1540 (δ_{N-H}), 1462 ($v_{C=C}$), 1304 (v_{C-N}), to the 2-aminobenzimidazole fragment. The IR spectrum of ligand **2** also shows bands assigned to the ferrocenyl ($v_{C=O}$ at 1678 cm^{-1}) and the 2-aminobenzimidazole units ($v_{C=N}$ at 1654, δ_{N-H} at 1540, $v_{C=C}$ at 1479 and 1462 and v_{C-N} at 1346, 1304 cm^{-1}). A band at 3415 cm^{-1} was assigned to the NH stretching mode.

The aromatic region of ^{1}H NMR spectrum of **1** in CDCl$_3$ shows two doublets at 7.29 and 6.93 ppm, and two triplets at 7.06 and 6.81 ppm assigned, respectively, to the Ha, Hd, Hb and Hc protons of the benzimidazole fragment (see Scheme 1). A broad signal at 6.45 is assigned to the NH_2 protons. Another set of signals are observed upfield, two multiplets at 4.89 and 4.53 ppm the for the α and β protons of the substituted cyclopentadienyl unit and one singlet at 4.22 ppm assigned to the unsubstituted cyclopentadienyl ring. These are consistent with the COSY spectrum. The ^{1}H NMR spectrum of **2** is similar, but three additional resonances from the additional ferrocenyl unit are observed. The aromatic protons of the benzimidazole ring resonate in the 7.32–6.85 ppm region, while the NH proton appears as a broad signal at 6.21 ppm. The chemi-

cal shifts of the ferrocenyl protons at 4.89, 4.55 and 4.20 ppm, are very close to those of **1**, and to those of the additional ferrocenyl fragment (4.83, 4.49 from α and β protons of the Cp ring and 4.30 ppm, from the unsubstituted Cp). The ^{13}C NMR spectra of compounds **1** and **2** are consistent with the proposed formulation, the assignments being based in HMQC spectra.

The liquid secondary mass spectra (LSIMS$^+$) of compounds **1** and **2** show the molecular peaks at $m/z = 345$ (**1**, 100%) and 558 (**2**, 8%), respectively.

The crystal structure of compound **1** has been established by X-ray diffraction studies and the molecule is shown in Fig. 1. Selected bonds lengths and angles are collected in Table 1. Complex **1** crystallizes in the monoclinic space group $C2/c$. The relative conformation of the Cp-rings is almost eclipsed; the torsion angle C(1)–X(1)–X(2)–C(6) is 0.9° (X(1) and X(2) represent the centroids of the Cp-rings C(1–5) and C(6–10), respectively). The benzimidazole fragment is almost ideally planar (mean deviation from plane 0.0198 Å). The interplanar angle between the substituted cyclopentadienyl ring and the benzimidazole group is 48.3°. The distances and angles of the benzimidazole fragment compare well with those reported for the compound 1-(ferrocenylmethyl)benzimidazole, [FcCH$_2$Bim] [22].
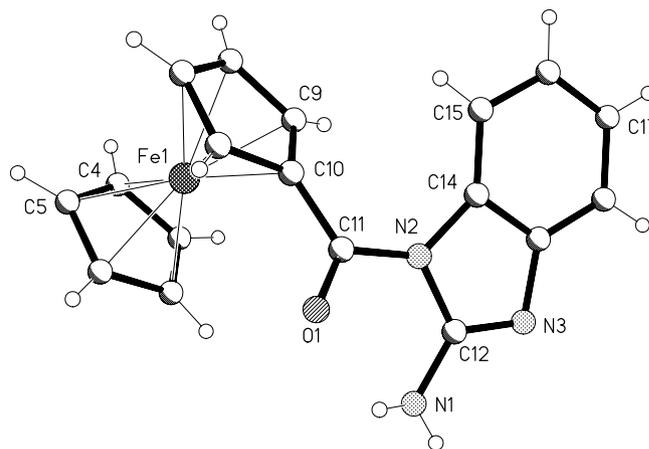
Fig. 1. Structure of compound **1** in the crystal with the atom numbering scheme. Radii are arbitrary.
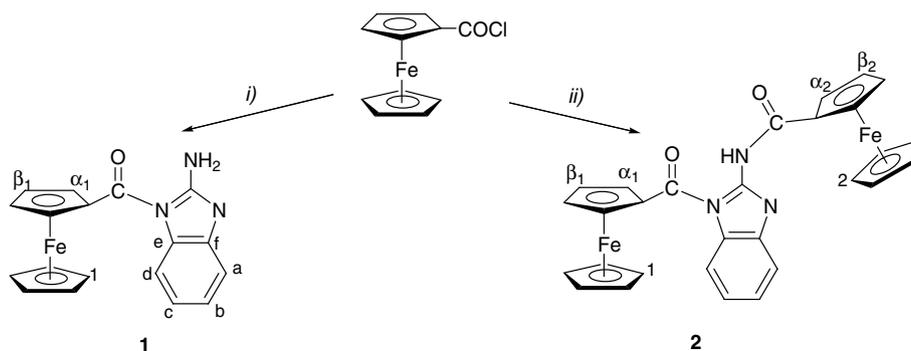
Scheme 1. (i) 2-aminobenzimidazole + NEt$_3$, (ii) 1/2 2-aminobenzimidazole + NEt$_3$.

Table 1
Selected bond lengths (Å) and angles (°) for compound **1**

N(1)–C(12)	1.337(3)	N(3)–C(13)	1.397(3)
N(2)–C(12)	1.403(3)	O(1)–C(11)	1.210(3)
N(2)–C(11)	1.415(3)	C(10)–C(11)	1.461(3)
N(2)–C(14)	1.416(3)	C(13)–C(14)	1.397(3)
N(3)–C(12)	1.307(3)		
C(12)–N(2)–C(11)	123.41(18)	O(1)–C(11)–C(10)	122.8(2)
C(12)–N(2)–C(14)	105.62(17)	N(2)–C(11)–C(10)	117.7(2)
C(11)–N(2)–C(14)	130.76(19)	N(3)–C(12)–N(1)	125.4(2)
C(12)–N(3)–C(13)	105.23(18)	N(3)–C(12)–N(2)	113.20(19)
O(1)–C(11)–N(2)	119.5(2)	N(1)–C(12)–N(2)	121.2(2)

Table 2
Hydrogen bonds for compound **1** (Å and °)

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
C(15)–H(15)...O(1)#1	0.94(2)	2.56(2)	3.308(3)	137.2(17)
N(1)–H(12)...N(3)#2	0.78(3)	2.19(3)	2.964(3)	178(3)
N(1)–H(11)...O(1)	0.81(3)	2.12(3)	2.710(3)	129(2)

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

In the crystal, the molecules are associated into pairs through two short hydrogen bonds involving one of the N–H functions of the NH_2 group and the N of the imidazole ring of the adjacent molecule (Fig. 2). The other N–H function forms an intramolecular H bond to O1. The molecules are further linked to form a 3D structure through C–H(benzimidazole)···O1 hydrogen bond (Table 2).

The reaction of the ferrocenylamidobenzimidazole ligand with several gold and silver compounds has been studied. Thus, the reaction of compound **1** with [Au(acac)(PPh₃)] occurs with deprotonation of the NH_2 group and coordination of the $AuPPh_3^+$ fragment giving the complex [Au{NH(benzim)COFc}(PPh₃)] (**3**) (see Scheme 2). The ^1H NMR spectrum shows the singlet and two multiplets attributable to the ferrocenyl protons, a singlet for the NH group and two doublets and two pseudo-triplets for the benzimidazole moiety. The $^{31}P\{^1H\}$ NMR spectrum presents one resonance for the phosphorus atom. In the mass spectrum (LSIMS+) the molecular peak appears at $m/z = 805$ (55%).

The reaction with other basic gold complex such as [O(AuPPh₃)₃]ClO₄ has been carried out and led to the deprotonation of the amino group and coordination of up to three gold(phosphine) units to the ligand. Two nitro-

gen atoms of the ligand are available for bonding, and a mixture of complexes is obtained. They consist of the mononuclear complex **3**, and two different trinuclear derivatives, where the gold atoms either coordinate to the amino nitrogen (**4a**), or to both the amino and the benzimidazole nitrogen atom (**4b**), as shown in Scheme 2. The outcome of this reaction can be followed in the $^{31}P\{^1H\}$ NMR spectrum, where a singlet for complex **3**, a singlet for compound **4a** and two singlets for compound **4b** appear. In the mass spectrum several fragments appear at $m/z = 1721$ ([Au₃{N(benzim)COFc}(PPh₃)₃]⁺, 8%), 1458 ([Au₃{N(benzim)COFc}(PPh₃)₂]⁺, 3%) and 1262 ([Au₂{N(benzim)COFc}(PPh₃)₂]⁺, 9%).

The reaction of compound **1** with Ag(OTf) affords the complex [Ag(OTf){FcCO (benzim)NH₂}] (**5**), in which the coordination of the silver atom probably takes place to the benzimidazole nitrogen atom. The several possibilities of coordination of the silver center to the ligand suggest that a supramolecular structure may be formed. The ^1H NMR spectrum shows resonances similar to those of the ligand and the gold complexes, but an upfield displacement is observed for the NH_2 protons. In the mass spectrum, the cation molecular peak appears at $m/z = 452$ (15%) and also the fragment Ag₂L⁺ at $m/z = 797$ (10%).

Finally, the reaction of the ferrocene–benzimidazole ligand with [Ag(OTf)(PPh₃)] has been carried out with
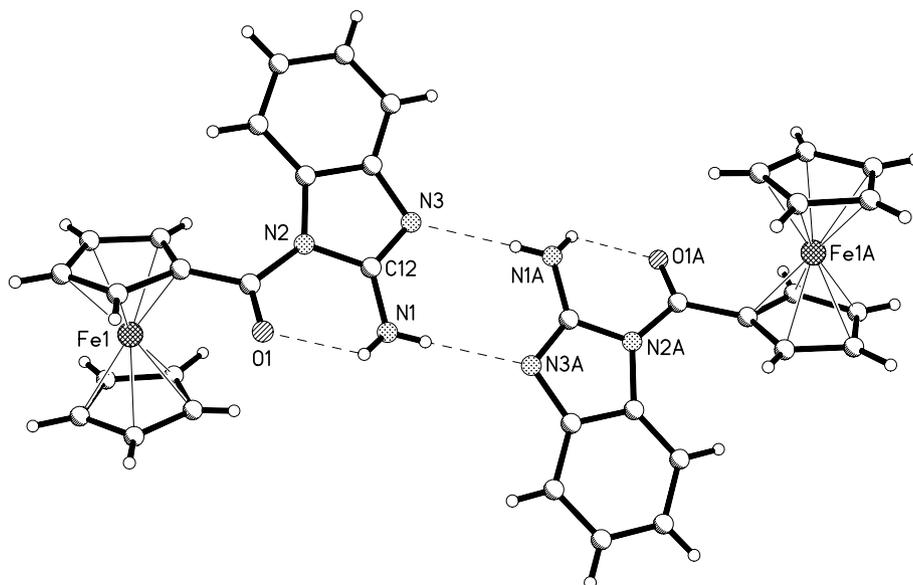
Fig. 2. Association of molecules in compound **1** through H bonding.
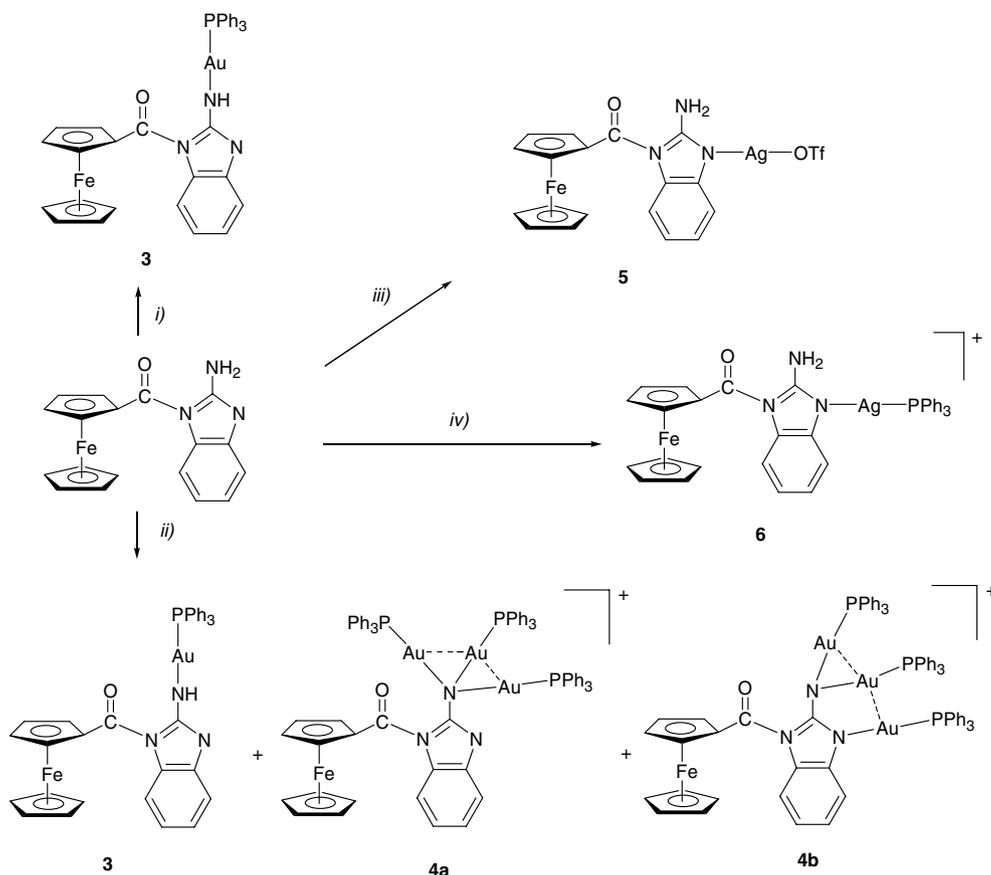
Scheme 2. (i) [Au(acac)(PPh$_3$)], (ii) [O(AuPPh$_3$)$_3$]ClO$_4$, (iii) Ag(OTf), (iv) [Ag(OTf)(PPh$_3$)].

formation of the complex [Ag(OTf){FcCO(benzim-NH$_2$)}(PPh$_3$)] (**6**). In the ^{1}H NMR resonances similar to those of complex **5** are observed, with the same upfield displacement of the NH$_2$ broad singlet, indicating coordination of the AgPPh$_3^+$ fragment to the benzimidazole nitrogen atom, as has been confirmed by an X-ray diffraction study. The mass spectrum shows the molecular peak at $m/z = 865$ (22%) and the cation molecular peak, [AgL(PPh$_3$)]$^+$, at $m/z = 714$ (37%).

The structure of complex **6** has been determined by X-ray diffraction studies and shows the presence of dimers in which the triflate anions act as bridging ligands, as depicted in Fig. 3 (the asymmetric unit consists of one molecule of the complex). Selected bonds lengths and angles are listed in Table 3. The silver atom adopts a strongly distorted tetrahedral environment; the angles around Ag range from 89.01(5)° [O(4)–Ag1–O(2)#2, #2 $-x+1$, $-y+2$, $-z+1$] to 143.74(5)° [N(2)–Ag1–P(1)]. The N–Ag–P angle is appreciably larger than the ideal tetrahedral angle, possibly reflecting the great steric effect of two bulky PPh$_3$ and FcCO(benzimNH$_2$) ligands. The silver atom lies 0.34 Å out of the plane formed by the atoms O(4), P(1) and N(2).

The benzimidazole fragment, almost ideally planar (mean deviation from plane 0.026 Å), has bond lengths and angles similar to those found in the uncoordinated
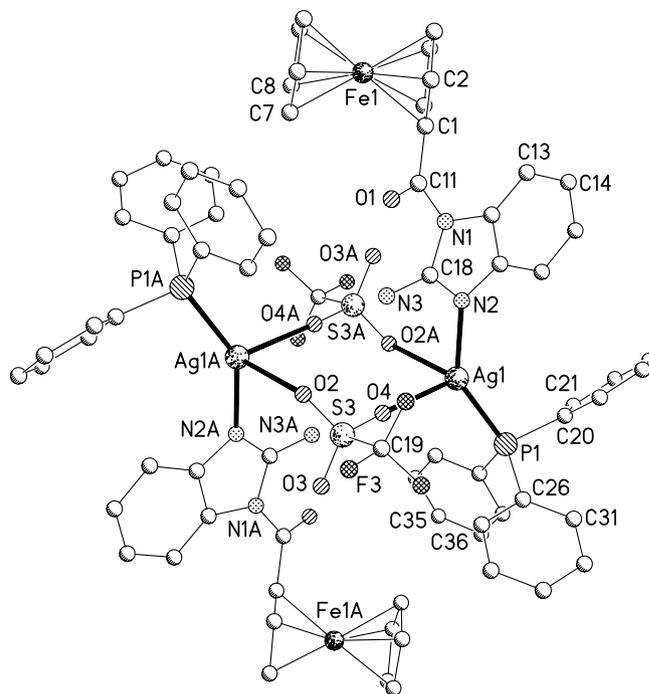
Fig. 3. Perspective view of compound **6** in the crystal.

ligand (compound **1**). The cyclopentadienyl rings deviate slightly from an eclipsed geometry [torsion angle C(1)–X(1)–X(2)–C(7) 4.6° (X(1) and X(2) represent the centroids

Table 3
Selected bond lengths (Å) and angles (°) for compound **6**

Ag(1)–N(2)	2.1840(16)	N(1)–C(18)	1.392(2)
Ag(1)–P(1)	2.3530(5)	N(1)–C(12)	1.412(2)
Ag(1)–O(4)	2.5092(16)	N(2)–C(18)	1.314(2)
Ag(1)–O(2)#2	2.6271(15)	N(2)–C(17)	1.397(2)
C(11)–O(1)	1.210(2)	N(3)–C(18)	1.324(3)
C(11)–N(1)	1.408(2)	C(12)–C(17)	1.392(3)
N(2)–Ag(1)–P(1)	143.74(5)	C(18)–N(1)–C(12)	106.38(16)
N(2)–Ag(1)–O(4)	96.16(6)	C(11)–N(1)–C(12)	129.45(16)
P(1)–Ag(1)–O(4)	112.57(4)	C(18)–N(2)–C(17)	106.12(16)
O(4)–Ag(1)–O(2)#2	89.01(5)	C(18)–N(2)–Ag(1)	131.26(14)
N(2)–Ag(1)–O(2)#2	89.87(6)	C(17)–N(2)–Ag(1)	122.38(13)
P(1)–Ag(1)–O(2)#2	111.42(4)	C(17)–C(12)–N(1)	105.10(16)
O(1)–C(11)–N(1)	120.02(17)	C(12)–C(17)–N(2)	110.28(17)
O(1)–C(11)–C(1)	124.36(18)	N(2)–C(18)–N(3)	125.78(19)
N(1)–C(11)–C(1)	115.62(16)	N(2)–C(18)–N(1)	112.10(17)
C(18)–N(1)–C(11)	124.07(16)	N(3)–C(18)–N(1)	122.10(18)

Symmetry transformations used to generate equivalent atoms: #2 $-x + 1$, $-y + 2$, $-z + 1$.

of the Cp-rings C(1–5) and C(6–10), respectively)]. The dihedral angle between the benzimidazole plane and Cp-rings are equal to 58.4°.

The Ag–O distances (2.5092(16) and 2.6271(15) Å) lie among the longest observed in literature for four-coordinated silver complexes [25–27]. The longer, 2.6271(15) Å Ag–O2#, indicates a weaker bond to the second triflate unit.

The Ag–N distance, 2.1840(16) Å, is shorter than those found in some tetracoordinated silver complexes, such as [$Ag_3(\mu$-bim)$_3$(PPh$_3$)$_5$] (from 2.290(5) to 2.349(5) Å for the four-coordinated silver atoms) [28], [$Ag_2(pz)_2$(PPh$_3$)$_3$] (2.295(2) and 2.323(2) Å for the four-coordinated silver atom) [29], [Ag{HB(3,5-Me$_2$pz)$_3$}(PMePh$_2$)] (from 2.316(6) to 2.336(5) Å) [30] or the complexes [AgX-{Fe[C$_5$H$_4$CH(pz)$_2$]$_2$}]$_n$ (X = BF$_4$, PF$_6$, SO$_3$CF$_3$ and SbF$_6$) (from 2.225(3) to 2.420(4) Å) [31].

The Ag–P distance, 2.3530(5) Å, is similar to that reported for the complex [Ag{HB(3,5-Me$_2$pz)$_3$}(PMePh$_2$)] (2.336(2) Å) [30] but shorter than those found in [$Ag_3(\mu$-bim)$_3$(PPh$_3$)$_5$] or [$Ag_2(pz)_2$(PPh$_3$)$_3$] (from 2.4377(19) Å to 2.5315(19) Å for the four-coordinated silver atoms) [28,29] or other tetrahedral silver complexes such as [Ag(dppe)$_2$]NO$_3$ (range 2.488(3)–2.527(3) Å) [32]. In addition, complex **6** displays several intra- and intermolecular

Table 4
Hydrogen bonds for compound **6** (Å and °)

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
C(3)–H(3)...F(3)#1	0.95	2.53	3.408(3)	153.4
C(33)–H(33)...O(2)#2	0.95	2.57	3.513(3)	170.4
C(34)–H(34)...O(1)#3	0.95	2.57	3.411(3)	147.3
N(3)–H(3A)...O(1)	0.84(3)	2.11(3)	2.706(2)	127(2)
N(3)–H(3B)...O(2)	0.82(3)	2.56(3)	3.185(2)	134(2)
N(3)–H(3B)...O(4)	0.82(3)	2.27(3)	3.054(3)	161(3)
C(4)–H(4)...O(3)#1	0.95	2.41	3.196(3)	139.8

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

hydrogens bonds N–H⋯O, C–H⋯O and C–H⋯F, that are summarised in Table 4.

DFT calculations [33] (ADF program [34]; see Computational section for details) were performed in order to understand the preference for the dimeric arrangement consisting of two complex cations and two triflate ions. The phenyl rings in the phosphine were replaced by hydrogens in the model used, and several possible arrangements were studied, namely the model of complex **6** (**6m**) and the cation obtained after removing the triflate anion, [Ag{FcCO(benzimNH$_2$)}(PH$_3$)]$^+$ (**6m**$^+$).

The optimized structure of the **6m**$^+$ cation is shown in Fig. 4. The coordination of Ag is almost linear (N–Ag–P angle 171°), while the Ag–N and Ag–P distances are 2.110 and 2.361 Å, respectively. The Ag–P distance is very close to those observed in the X-ray structure (2.353 Å), but Ag–N is much shorter (exp 2.184 Å). Mayer indices (MI) [35], scaling as bond strength indicators, were calculated. For the Ag–N bond the MI drops from 0.315 in **6m**$^+$ to 0.249 in the X-ray structure (with PH$_3$ ligands). There is an intramolecular CO⋯H–N hydrogen bond, as observed in the X-ray structure of the ligand (Fig. 2).

The addition of one triflate anion leads to a lengthening of the Ag–N bond (2.202 Å, MI 0.273), while the Ag–P bond does not change, and the angle narrows to 142°. The new Ag–O bond is relatively short (2.358 Å, MI 0.221), the coordination geometry around Ag having become a wide Y. The binding energy of triflate to the **6m**$^+$ cation, forming **6m**, is −82.2 kcal mol^{-1}. Two new intramolecular hydrogen bonds (O⋯H distances of 1.879 Å) are established between the second N–H bond and two oxygen atoms of the triflate, including the one bound to silver. When a second triflate is added to **6m**, the binding energy is much lower but still attractive (−15.6 kcal mol^{-1}). This simple model suggests that silver has a tendency to achieve four coordination. The Ag environment is a very distorted tetrahedron, with angles ranging from 89° to 131° (N–Ag–P), the two triflate anions binding very differently. The two Ag–O distance are 2.340 and 2.697 Å (MI 0.211 and 0.105, respectively). The binding of the second OTf anion has resulted in further
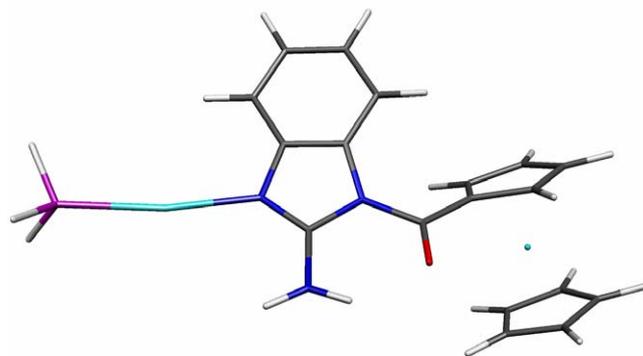
Fig. 4. Molekel representation of the [Ag{FcCO(benzimNH$_2$)}(PH$_3$)]$^+$ cation (**6m**$^+$).

weakening of the Ag–N bond (2.251 Å, MI 0.241), while the Ag–P bond remains unchanged. The intramolecular hydrogen bond network has also changed. Besides the C–O$\cdots$H–N bond, only one, but stronger, hydrogen bond is formed between the second N–H of the benzimidazole and the bound oxygen of the triflate (O$\cdots$H distance of 1.815 Å).

The X-ray structure consists of two units of **6**. In order to compare the values, single point calculations were performed on a structure similar to the experimental one but with phenyl groups replaced by hydrogen atoms. The energy of the optimized **6m** is much lower than that of the same fragment in the X-ray structure, essentially because the Ag–N and one of the Ag–O bonds are significantly shorter (and stronger) and the angles may adjust. Despite the slightly distorted geometry, the dimerization energy was calculated as -23.8 kcal mol^{-1} (difference between the energy of the dimer and twice the energy of the monomers). The Ag–N and Ag–O bond lengths adapt and Ag achieves a four coordination environment. On the other hand, the Ag-phosphine fragment remains very rigid. In the observed structure two sets of hydrogen bonds are also observed: one C–O$\cdots$H–N bond and one N–H$\cdots$O bond with the bound oxygen of the closest triflate (O$\cdots$H distance of 2.106 and 2.275 Å). Since hydrogen bonds are found in all models, they do not particularly contribute to stabilize any of the possible arrangements.

3. Experimental section

3.1. 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 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 a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in CDCl$_3$. Chemical shifts are cited relative to SiMe$_4$ (^{1}H, ^{13}C external), and 85% H$_3$PO$_4$ (^{31}P, external). Electronic spectra were recorded with a UNI-CAM model UV-4 spectrophotometer.

3.2. Materials

The starting materials FcCOCl [36], [Au(acac)(PPh$_3$)] [37], [O(AuPPh$_3$)$_3$]ClO$_4$ [38], and [Ag(OTf)(PPh$_3$)] [39] were prepared by published procedures. All other reagents were commercially available.

Safety note. Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

3.3. Synthesis

3.3.1. Synthesis of FcCO(benzimNH$_2$) (1)

To a solution of 2-amino-benzimidazole (1.335 g, 1 mmol) and NEt$_3$ (1.21 g, 1.2 mmol) in dichloromethane (20 mL) at 0 °C was added dropwise FcCOCl (0.247 g, 1 mmol). After the addition the mixture was allowed to reach room temperature and stirred for 12 h. Then solution was washed with a saturated solution of NaHCO$_3$ in water; the organic phase separated, dried over Na$_2$SO$_4$ and evaporated to ca. 2 mL. Addition of hexane gave compound **1** as a red solid. Yield: 55%, 0.190 g. Λ_M 3.3 Ω^{-1} cm^2 mol^{-1}. Elemental analysis (%), Found: C, 62.61; H, 4.23; N, 12.12. Calc. for C$_{18}$H$_{15}$FeN$_3$O (345.176): C, 62.63; H, 4.38; N, 12.17. NMR data: ^{1}H NMR (ppm): 4.22 (s, 1-C$_5$H$_5$, 5H), 4.53 (m, β_1-C$_5$H$_4$, 2H), 4.89 (m, α_1-C$_5$H$_4$, 2H), 6.45 (br, NH$_2$), 6.81 (t, Hc, 1H), 6.93 (d, Hd, 1H), 7.06 (t, Hb, 1H), 7.29 (d, Ha, 1H). ^{13}C NMR (ppm): 172.90 (C=O), 154.08 (C-NH$_2$), 142.04 (Ce), 131.44 (Cf), 123.86 (Cb), 120.09 (Cc), 116.58 (Ca), 113.14 (Cd), 73.76 ($\underline{C}$(Cp)-C=O), 72.55 (Cα_1, C$_5$H$_4$), 72.37 (Cβ_1, C$_5$H$_4$), 71.04 (1-C$_5$H$_5$). UV/Vis (CH$_2$Cl$_2$): 470 nm

3.3.2. Synthesis of (FcCO)$_2$(NHbenzim) (2)

To a solution of 2-amino-benzimidazole (1.335 g, 1 mmol) and NEt$_3$ (1.21 g, 1.2 mmol) in dichloromethane (20 mL) at 0 °C was added dropwise FcCOCl (0.494 g, 2 mmol). After the addition the mixture was allowed to reach room temperature and stirred for 12 h. Then solution was washed with a saturated solution of NaHCO$_3$ in water; the organic phase separated, dried over Na$_2$SO$_4$ and evaporated to ca. 2 mL. Addition of hexane gave compound **2** as a red solid. Yield: 67%, 0.374 g. Λ_M 3.0 Ω^{-1} cm^2 mol^{-1}. Elemental analysis (%), Found: C, 62.31; H, 4.09; N, 7.56. Calc. for C$_{29}$H$_{23}$Fe$_2$N$_3$O$_2$ (557.202): C, 62.51; H, 4.16; N, 7.54. NMR data. ^{1}H NMR (ppm): 4.20 (s, 1-C$_5$H$_5$, 5H), 4.30 (s, 2-C$_5$H$_5$, 5H), 4.49 (m, β_2-C$_5$H$_4$, 2H), 4.55 (m, β_1-C$_5$H$_4$, 2H), 4.83 (m, α_1-C$_5$H$_4$, 2H), 4.89 (m, α_2-C$_5$H$_4$, 2H), 6.21 (br, NH), 6.85 (t, Hc, 1H), 6.95 (d, Hd, 1H), 7.09 (t, Hb, 1H), 7.32 (d, Ha, 1H). ^{13}C NMR (ppm): 172.80 (C=O), 167.64 (C'=O), 154.05 (C–NH), 141.84 (Ce), 131.27 (Cf), 123.76 (Cb), 119.09 (Cc), 116.42 (Ca), 113.05 (Cd), 73.62 ($\underline{C}$(Cp)-C=O), 72.75 ($\underline{C}$(Cp)-C'=O), 72.65 (β_2-C$_5$H$_4$), 72.43 (α_1-C$_5$H$_4$), 72.28 (β_1-C$_5$H$_4$), 70.94 (1-C$_5$H$_5$), 70.74 (α_2-C$_5$H$_4$), 70.13 (2-C$_5$H$_5$). UV/Vis (CH$_2$Cl$_2$): 464 nm

3.3.3. Synthesis of [Au(PPh$_3$){NH(benzim)COFc}]ClO$_4$ (3)

To a solution of **1** (0.035 g, 0.1 mmol) in dichloromethane (20 mL) was added [Au(acac)(PPh$_3$)] (0.056 g, 0.1 mmol). The mixture was stirred for 2 h. Then solution was evaporated to ca. 5 mL and addition of hexane gave compounds **3** as a orange solid. Yield: 58%, 0.047 g. Λ_M 9.4 Ω^{-1} cm^2 mol^{-1}. Elemental analysis (%), Found: C, 53.41; H, 3.52; N, 5.37. Calc. for C$_{36}$H$_{29}$FeAuPN$_3$O (803.42): C, 53.82; H, 3.64; N, 5.23. NMR data. ^{1}H

NMR (ppm): ^{1}H, δ: 4.27 (s, 5H, C_5H_5), 4.60 (m, 2H, C_5H_4), 4.95 (m, 2H, C_5H_4), 5.95 (br, 1H, NH), 6.90 (m, 1H, benzim), 7.0 (m, 1H, benzim), 7.15 (m, 1H, benzim), 7.34 (m, 1H, benzim), 7.37–7.65 (m, 15H, Ph), ppm. ^{31}P–{^{1}H} (ppm): 33.46 (s, 1P, PPh$_3$).

3.3.4. Synthesis of [(AuPPh$_3$)$_3${N(benzim)COFc}] (4a and 4b)

To a solution of compound **1** (0.035 g, 0.1 mmol) in dichloromethane (20 mL) was added [O(AuPPh$_3$)$_3$]ClO$_4$ (0.149 g, 0.1 mmol). The mixture was stirred for 3 h. Then solution was evaporated to ca. 5 mL and addition of diethyl ether gave a mixture of complexes **4a** and **4b** as yellow-orange solids. NMR data. ^{31}P–{^{1}H} (ppm): 33.46 (s, 1P, PPh$_3$, complex **3**), 32.6 (s, 3P, PPh$_3$, complex **4a**), 31.7 (s, 2P, PPh$_3$, complex **4b**), 27.9 (s, 1P, PPh$_3$, complex **4b**).

3.3.5. Synthesis of [Ag(OTf){FcCO(benzim)NH$_2$}] (5)

To a solution of compound **1** (0.035 g, 0.1 mmol) in dichloromethane (20 mL) was added Ag(OTf) (0.026 g, 0.1 mmol). The mixture was stirred for 3 h. Then solution was evaporated to ca. 5 mL and addition of diethylether gave compound **5** as an orange solid. Yield: 91%, 0.055 g. Λ_M 84 Ω^{-1} cm^2 mol^{-1}. Elemental analysis (%), Found: C, 37.59; H, 2.49; N, 6.43; S, 5.21. Calc. for $C_{19}H_{15}F_3FeAgN_3O_4S$ (602.114): C, 37.90; H, 2.51; N, 6.98; S, 5.32. NMR data. ^{1}H NMR (ppm): ^{1}H, δ: 4.0 (br, 2H, NH$_2$), 4.30 (s, 5H, C_5H_5), 4.75 (m, 2H, C_5H_4), 4.96 (m, 2H, C_5H_4), 7.09 (m, 1H, benzim), 7.32 (m, 1H, benzim), 7.40 (m, 1H, benzim), 7.87 (m, 1H, benzim).

3.3.6. Synthesis of [Ag(OTf){FcCO(benzim)NH$_2$}(PPh$_3$)] (6)

To a solution of compound **1** (0.035 g, 0.1 mmol) in dichloromethane (20 mL) was added [Ag(OTf)(PPh$_3$)] (0.043 g, 0.1 mmol). The mixture was stirred for 1 h and then the solvent was evaporated to ca. 5 mL and addition of diethylether gave compound **6** as an orange solid. Yield: 67%, 0.057 g. Λ_M 111 Ω^{-1} cm^2 mol^{-1}. Elemental analysis (%), Found: C, 51.09; H, 3.28; N, 4.56; S, 3.72. Calc. for $C_{37}H_{30}F_3FeAgN_3O_4PS$ (864.40): C, 51.41; H, 3.49; N, 4.86; S, 3.71. NMR data. ^{1}H NMR (ppm): 3.8 (br, 2H, NH$_2$), 4.33 (s, 5H, C_5H_5), 4.75 (m, 2H, C_5H_4), 4.96 (m, 2H, C_5H_4), 7.11 (m, 1H, benzim), 7.25–7.53 (m, 15H, Ph), 7.55 (m, 1H, benzim), 7.67 (m, 1H, benzim), 7.97 (m, 1H, benzim). ^{31}P–{^{1}H} (ppm): 12.2 (s, br, 1P, PPh$_3$).

3.4. X-ray crystallography

The crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the Bruker SMART CCD diffractometer. Crystal data and details of data collection and structure refinement are given in Table 5. Absorption corrections were based on multiple scans (program SADABS). The structures were refined on F^2 using the program SHELXL-97 [40]. All non-hydrogen atoms were

Table 5
Details of data collection and structure refinement for complexes **1** and **6**

Compound	1	6
Chemical formula	$C_{18}H_{15}FeN_3O$	$C_{37}H_{30}AgF_3FeN_3O_4PS$
Crystal habit	Orange prism	Red prism
Crystal size (mm)	$0.38 \times 0.20 \times 0.10$	$0.44 \times 0.24 \times 0.20$
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	18.2850(19)	12.4837(9)
b (Å)	8.6986(9)	12.5587(9)
c (Å)	20.295(2)	13.1468(10)
α (°)	90	62.4930(10)
β (°)	114.000(2)	66.8840(10)
γ (°)	90	81.4210(10)
U (Å^3)	2948.8(5)	1680.1(2)
Z	8	2
D_c (g cm^{-3})	1.555	1.709
M	345.18	864.39
$F(000)$	1424	872
T (°C)	−173	−173
$2\theta_{max}$ (°)	57	57
μ(Mo Kα) (mm^{-1})	1.030	1.188
Transmission	0.81461, 1.00000	0.6230, 0.7971
Number of reflections measured	9316	15463
Number of unique reflections	3410	7609
R_{int}	0.0365	0.0188
R^a ($F > 4\sigma(F)$)	0.0400	0.0286
wR_2^b (F^2, all refl.)	0.0900	0.0730
Number of reflections used	3410	7609
Number of parameters	268	468
Number of restraints	0	0
S^c	0.971	1.020
Max. $\Delta\rho$ (e Å^{-3})	0.786	0.966

^{a} $R(F) = \sum ||F_o| - |F_c||/\sum |F_o|$.
^{b} $wR(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$; $w^{-1} = s^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.
^{c} $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

refined anisotropically. Hydrogen atoms were included using a riding model.

3.5. Computational details

Density functional calculations [33] were carried out with the Amsterdam Density Functional program (ADF2005) [34]. Gradient corrected geometry optimizations, [41] [C] without any symmetry constraints, were performed using the the Local Density Approximation of the correlation energy (Vosko, Wilk and Nusair's) [42] [D] and the Generalized Gradient Approximation (Perdew–Wang [43] [E] exchange and correlation corrections). A triple-ζ Slater-type orbital (STO) basis set augmented by one polarization function was used for all atoms. A frozen core approximation was used to treat the core electrons: (1s) for C, N, F and O; ([1–2]s, 2p) for S, P and Fe; ([1–3]s [2–3]p 3d) for Ag. Relativistic effects were treated with the ZORA approximation [44]. [F] Mayer indices [35] were calculated and used as bond strength indicators. Three-dimensional representations of molecules were obtained

with Molekel [45]. The models were based on the X-ray structure described in this work for complex **6**, with the phenyl rings of the phosphines replaced by hydrogen atoms.

Acknowledgements

Appendix A. Supplementary data

CCDC-278148 and 278149 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.htlm [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223 336033; e-mail; deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.025.

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