A cytotoxic bis(carbene)gold(I) complex of ferrocenyl complexes: synthesis and structural characterisation†

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The N-heterocyclic carbene (NHC) precursors 1-[(*E*)-2-butenyl]-3-(4-ferrocenylphenyl)imidazolium bromide (**2**) and 1-[(*E*)-2-butenyl]-3-(4-ferrocenylphenyl)imidazolium tetrafluoroborate (**3**) were derived from 1-(4-ferrocenylphenyl)imidazole. Ferrocenyl complex **3** reacts with Ag_2O and chloro(dimethylsulfide)gold(I) in the presence of tetraethylammonium chloride to produce the mixed metal species bis{1-[(*E*)-2-butenyl]-3-(4-ferrocenylphenyl)-2*H*-imidazol-2-ylidene}gold(I) tetrafluoroborate (**4**). Single crystal X-ray structure analyses of **1**, **3** and **4** indicate that the NCHN-hydrogen in **3** is hydrogen bonded to the BF_4^- anion [C(H1)···F, 3.265(4) Å], as is also reflected in the position of its ^{1}H NMR chemical shift. Cytotoxicity studies show that complex **4** is selective for cancer cells and active against the tumour cell lines Jurkat and MCF 7.

Introduction

Three of the main approaches for the preparation of gold carbene complexes include (i) nucleophilic addition of alcohols or amines to gold-coordinated isocyanides,[1] (ii) transfer from Fischer-type alkoxy-organo or amino-organo carbene complexes of group 6 metals to form gold(I) and gold(III) complexes,[2,3] and (iii) deprotonation or activation of N-heterocyclic compounds (NHC) before coordination to a gold center.[4]

The activation strategies used for the preparation of NHC–metal complexes can be divided into (i) cleavage of the C=C bond of electron-rich alkenes,[5] (ii) generation of a free carbene by deprotonation of the corresponding imidazolium precursor with a strong base (for example with BuLi, NaH or *t*-BuOK),[6] (iii) transmetallation of a deprotonated azole followed by protonation or alkylation of the gold azolyl compounds[7] [lithiated imidazoles mainly form bis(carbene) complexes with gold(I)],[8] (iv) *in situ*-deprotonation of an imidazolium salt with a weak base (for example NEt_3 or OAc^-)[9,10] and (v) transmetallation from a silver–NHC complex prepared by the direct reaction of an imidazolium precursor with Ag_2O.[11,12]

Our interest in investigating the possible uses of NHC ligands in the synthesis of new biologically-active gold(I) compounds as alternatives to gold(I) phosphines was sparked by recent articles by Baker *et al.*[13] and Barnard *et al.*[10] which involved the synthesis of gold(I) complexes of NHCs as potential anti-mitochondrial and thus anti-tumour agents. Previously all gold(I) compounds with anti-tumour activity contained phosphine ligands[14] and although gold(I) phosphine compounds are known for their anti-tumour potential it is also known that the phosphine ligands on their own show anti-tumour activity which increases when complexed to gold. Although initial studies of the mechanism of anti-cancer activity in gold complexes pointed towards DNA as the target, subsequent studies of gold(I) carbene complexes with potential anti-tumor activity showed that they rather target mitochondrial membranes. Similarly, Au(III) cyclometalated complexes do not cross-link DNA like cisplatin, indicating a different mechanism of action. The analogy of d^8 square planar Au(III) and Pt(II) complexes does not extend to their interaction with cells.[15] The influence of the phosphine ligand on the activity of a gold(I) complex remains unexplored.

A number of studies of gold(I) complexes linked to ferrocene derivatives, with the common denominator being that they contain gold(I) phosphines or *P*-substituted ferrocene ligands, underline the fact that such compounds exhibit significant cytotoxic effects.[16–20] Further examples of phosphine-free, ferrocene-containing complexes were described by Gimeno *et al.*,[21] who studied the gold(I) complexes $[Fe(C_5H_4S_2\text{-}CNEt_2)_2(AuCl)_2]$[22] and $[AuX(pzCH_2Fc)]$ (X = Cl or C_6F_5; $pzCH_2Fc$ = ferrocenylmethylpyrazole),[23] and one gold(III) complex: $[Au(C_6F_5)_3(pzCH_2Fc)]$.[23]

One of the most general strategies for introducing a large diversity of arene-spacered functionalities onto ferrocene is the Gomberg–Bachmann–Hey arylation, as previously described for carboxylic acids,[24–26] carboxylic acid esters,[27]

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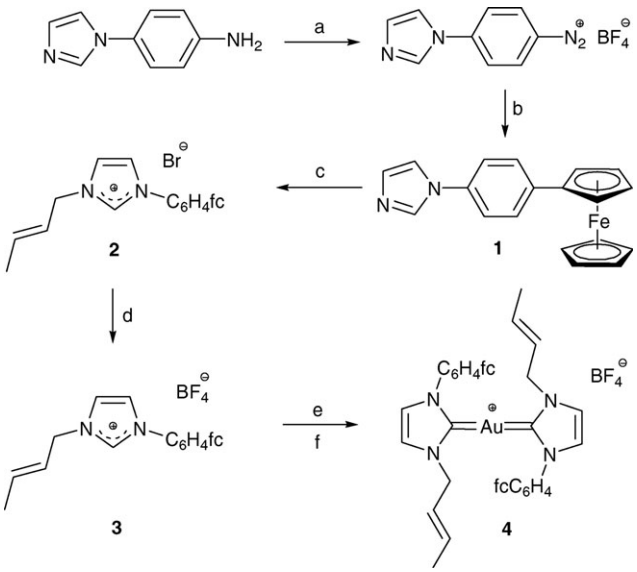

Scheme 1 Preparation of compounds **1–4**: (a) $NaNO_2$, HBF_4; (b) ferrocene; (c) 1-bromo-2-butene; (d) NH_4BF_4; (e) Ag_2O, $[NEt_4]Cl$; (f) Me_2SAuCl.

nitrophenyls,[28] halophenyls,[24–25,29] mercaptophenyls[30] and terminal phenylacetylenes.[31] The same concept can also be applied to the conjugative attachment of imidazoles in order to access electrophoric NHC complexes, which have received attention as redox responsive model systems.[32–36] Our main target, **4**, is a phosphine-free bis(carbene) complex of gold, carrying an electrophoric, cytotoxic ferrocene moiety. A preliminary study regarding the cytotoxic activity of **4** has been undertaken, and the characterisation of the two precursors, **1** and **3**, are also reported here.

Results and discussion

A Gomberg arylation, depicted in Scheme 1, using diazotation and coupling with ferrocene afforded precursor **1**. Alternatively, an equimolar reaction of 4-(1*H*-imidazolyl)phenyldiazonium bis(hexafluorophosphate) with ferrocene, followed by treatment with $NaHCO_3$, also yielded **1**.† Subsequent alkylation with 1-bromo-2-butene in CH_2Cl_2 yielded the hygroscopic NHC precursor 1-[(*E*)-2-butenyl]-3-(4-ferrocenylphenyl)imidazolium bromide (**2**), and after anion metathesis in acetone, 1-[(*E*)-2-butenyl]-3-(4-ferrocenylphenyl)imidazolium tetrafluoroborate (**3**) was obtained. The bis(carbene) gold(I) complex **4** was generated by reaction of **3** with Ag_2O and subsequent carbene ligand transfer to $(CH_3)_2SAuCl$. Attempts to synthesise the bis(carbene) according to alternative method (iii), mentioned above, failed. Carbene complex **4** is stable in air and decomposes only slowly in solution when exposed to air.

Nuclear magnetic resonance

The ^1H NMR spectra of the new precursor compounds **1–3** and the complex product **4** are very similar to those of the corresponding free organic ligand. The most active proton in the azole ring, H1 (Fig. 1), is extremely sensitive towards changes in the ring, and its chemical shift changes from δ 8.08 in **1** to δ 11.16 in the cation **2**, and then again upfield to δ 9.21 in **3**, when only the counterion is changed. A similar shielding of the NCHN proton by the close proximity of the anion of 1-[prop-2-ynyl]-3-vinyl-1*H*-imidazolium tetraphenylborate to this proton was recently investigated by NMR studies and a crystal structure determination.[37] The crystal structure determination of **3** shows hydrogen bonding between H1 and an F atom on BF_4^- (*vide infra*). The assignments of the signals observed for **4** in CD_2Cl_2 were unambiguously confirmed by gHSQC and ^1H,^{13}C gHMQC measurements. No NCHN signal is present, indicating successful deprotonation of the azole unit with Ag_2O, and a sharp singlet at δ 182.5 for the carbene carbon confirms that metallation has occurred. Similar chemical shifts have been reported for related NHC complexes of gold.[10] The signals for the NCH=CHN protons appear in the ^1H NMR spectra between δ 7.62 and 7.14 for **1–4**. The same carbon atoms resonate at δ 132.3 and 129.9 in the ^{13}C NMR spectrum of **1**, and are shielded by more than $\Delta\delta$ 8 in the spectra of **2–4**, when compared to **1**.

The signals of the unsubstituted cyclopentadienyl rings in **2–4** are essentially unchanged at *ca.* δ 4.06 in their ^1H NMR spectra and at *ca.* δ 70 in their ^{13}C NMR spectra. The protons of the monosubstituted cyclopentadienyl ring appear at δ 4.81 and 4.38 in **1**, and at *ca.* δ 4.7 and 4.4 in **2–4** as an unsymmetrical pair of triplets, indicating an A_2B_2 system with $^3J = {}^4J$, where protons H2A and H5A are deshielded by the aromatic phenyl ring bearing the ferrocenyl substituent. The cyclopentadienyl carbon connected to the phenyl substituent is significantly deshielded at *ca.* δ 83, while the other carbons in the same ring are observed at *ca.* δ 67. The butenyl CH_2 protons (H12) and carbons (C12) of **2** and **3** have the expected chemical shifts.

Infrared spectroscopy

The IR spectra of all new compounds have very similar patterns, and the presence of the BF_4^- anion in **3** and **4** is confirmed by very intense bands between 1032 and 1107 cm^{-1}.

Mass spectrometry

The molecular ion of **1** (EI-MS) and the cations of **2–4** (FAB-MS) were present in mass spectra of the compounds. The most characteristic peak in the mass spectrum of **4** corresponds to the $[M - BF_4]^+$ fragment (m/z = 961), and another peak representing the [cation-Fc]$^+$ fragment (Fc = ferrocenyl) (m/z = 777) is also observed.

Crystallography

Compounds **1**, **3** and **4** furnished crystals suitable for X-ray diffraction studies. Table 1 summarises selected bond lengths and angles. All the dihedral angles between the planes in **1–4** are reported in Table 2. The molecular structure of **1** is shown in Fig. 1.‡ It crystallises in the monoclinic space group $P2_1/c$ with one molecule in the unit cell and consists of a ferrocenyl group appended to a phenyl-imidazolium moiety in the *para*-position. The η^5-C_5H_4 cyclopentadienyl ring of the ferrocene moiety is influenced by the phenyl-imidazolium substituent,

‡ For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713917a

Table 1 Selected bond angles (°) and distances (Å) for compounds **1**, **3** and **4**

	1	3	4
C1–N2	1.330(2)	1.327(4)	1.33(1)
N2–C3	1.381(2)	1.376(4)	1.39(1)
C3–C4	1.330(2)	1.343(4)	1.35(1)
C4–N5	1.3703(2)	1.390(4)	1.39(1)
N5–C1	1.371(2)	1.332(4)	1.337(9)
C9–C1A	1.473(2)	1.477(4)	1.48(2)
N5–C6	1.425(2)	1.446(4)	1.42(1)
N2–C12		1.484(4)	1.45(1)
Au1–C1			2.021(8)
C1–Au1–C1′			179.997(1)
N2–C1–N5	109.4(2)	108.4(3)	106.2(7)

Table 2 Dihedral angles (°) between planes for compounds **1**, **3** and **4**

	1	3	4
A and B	12.6(1)	13.82(4)	2.3(7)
B and C	24.34(9)	20.35(6)	50.2(3)
A and C	13.3(1)	6.53(7)	52.3(4)

Planes defined by atoms: A: C1A–C2A–C3A–C4A–C5A; B: C6–C7–C8–C9–C10–C11; C: C1–N2–C3–C4–N5.

leading to a distorted angle of 106.69(13)° for C2A–C1A–C5A. The phenyl ring is twisted 12.6(1)° away from the least-square plane of the cyclopentadienyl ring defined by C1A–C2A–C3A–C4A–C5A and 24.34(9)° from the azole unit defined by C1–N2–C3–C4–N5. Furthermore, the plane of the azole unit is rotated by 13.3(1)° with respect to the η^5-C_5H_4 plane. The heterocyclic group experiences a 1 : 1 occupation disorder at two positions, N2═C3b and C3═N2b. The molecular packing of **1** along the crystallographic c-axis is shown in Fig. 2. In broad descriptive terms, when viewed down the c-axis, the molecules in the unit cell are arranged in such a way that every second molecule is turned by 90°. This leads to an infinite chain, with the different layers packed in opposite directions and no intermolecular bonding between adjacent chains.

Crystals of **3** crystallise in the monoclinic space group $P2_1/n$, and Fig. 3 illustrates this alkylated product of **1** in the form of its BF_4^- salt.‡ The two cyclopentadienyl rings are now planar and parallel, with a torsion angle of 0.2° for C1A–center–center–C6A. The whole ferrocene unit remains unaffected by the alkylation. The angle between the plane of the η^5-C_5H_4 ring and the plane of the phenyl moiety, when compared to **1**,

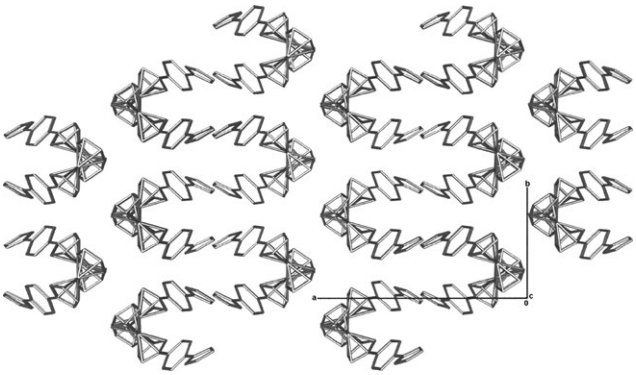

Fig. 2 Packing diagram of **1** in the unit cell, shown along the c-axis; hydrogen atoms are omitted for clarity.

is practically unchanged (difference only 1.2°). The BF_4^- counterion is sandwiched between butenyl chains of neighbouring molecules. Lattice organisation is governed by hydrogen bonding of the BF_4^- counterion with the H atoms of molecules in different layers. Such contacts, listed in Table 3, involve the heterocyclic rings (C1–H1), the C_6H_4 group (C7–H7), the butenyl group (C12–H12B), as well as the NCH═C(H)N fragment (C4–H4) and a C_6H_4 unit (C11–H11) of neighbouring molecules.

The molecular structure of **4**, shown in Fig. 4, features crystallographic inversion symmetry at the gold centre.‡ Compound **4** crystallises in the trigonal space group *R*-3. The asymmetric unit contains the gold complex, a highly disordered BF_4^- anion and a solvent molecule, CH_2Cl_2. The structure reveals the linear coordination of the central gold atom to the two carbene carbons, with a C1–Au–C1′ angle of 180°. The Au–$C_{carbene}$ bond lengths of 2.021(8) Å are similar to reported values in other essentially comparable compounds, such as bis[μ-[2,6-pyridinediylbis[methylene(3-methyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene)]]]digold dibromide [Au–$C_{carbene}$ = 2.024(8) and 2.017(8) Å].[10]

As in **3**, both cyclopentadienyl rings are almost parallel, with a torsion angle of 2.9° for C1A–center–center–C6A. The ferrocene unit is not changed by carbene formation. However, large differences are found for the dihedral angles between the planes of the different connected rings. The η^5-C_5H_4 ring and the phenyl ring are now nearly parallel, but the azole unit, defined by C1–N2–C3–C4–N5, is twisted by 52.3(4)° from the η^5-C_5H_4 ring. This large tilt results from the linear orientation of the C–Au–C arrangement. The BF_4^- counterions are

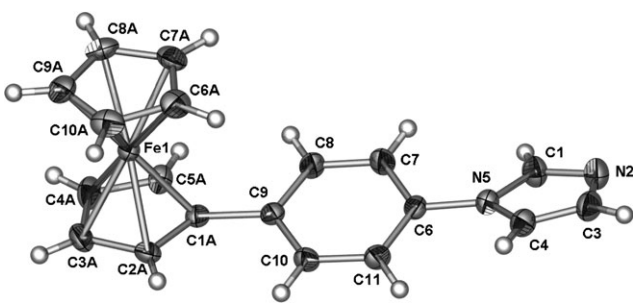

Fig. 1 Molecular structure of **1** showing the numbering scheme. The thermal ellipsoids are depicted at 50% probability.

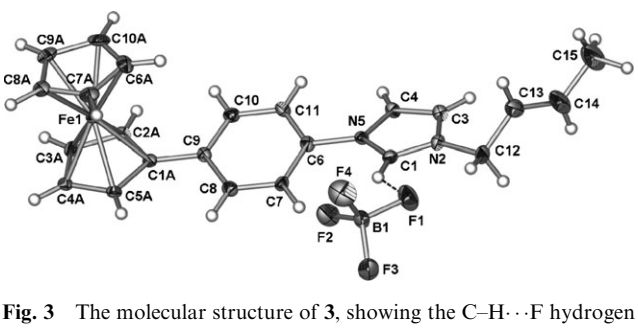

Fig. 3 The molecular structure of **3**, showing the C–H···F hydrogen interaction. The thermal ellipsoids are scaled to the 50% probability level.

Table 3 C–H···F hydrogen geometry (Å, °) in compound **3**

C–H···F	<(C–H···F)	*d*(C–H)	*d*(H···F)	*d*(C···F)
C1–H1···F1[a]	136	0.95	2.51	3.265(4)
C1–H1···F2[a]	164	0.95	2.32	3.247(4)
C4–H4···F3[b]	170	0.95	2.17	3.110(4)
C7–H7···F2[a]	139	0.95	2.52	3.297(4)
C11–H11···F3[b]	152	0.95	2.45	3.314(4)
C12–H12B···F1[a]	154	0.99	2.38	3.297(4)

Symmetry codes:[a] $-x+1, -y+1, -z+1$. [b] $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

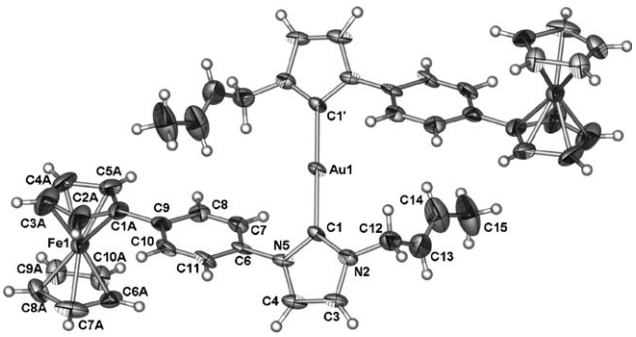

Fig. 4 The molecular structure of **4** showing the numbering scheme. The symmetry code for atom C1′ is $(-x+\frac{1}{3}, -y+\frac{2}{3}, -z+\frac{2}{3})$. Only crystallographically unique atoms are labelled; the BF_4^- anion and a CH_2Cl_2 molecule are omitted for clarity. The thermal ellipsoids are depicted at 40% probability.

involved in hydrogen bonding and the boron atoms are located on a 3-fold rotation axis (site occupancy factor 1/3) with well ordered positions of the fluorine atoms and on the center of a 3-fold rotoinversion axis (site occupation 1/6) leading to positional disorder of fluorine atoms. The lattice organisation is dominated by C–H···F interactions between the anion, the complex itself and the CH_2Cl_2 solvent molecule, with relevant separations ranging from 3.030(19) to 3.326(12) Å (Table 5).

Cytotoxicity studies

Cytotoxicity assays were performed to establish the sensitivity of cancer cell lines and normal cell cultures to compound **4**, and are given in Table 4. Complex **4** was screened against the human HeLa cervix epithelioid carcinoma cell line, the CoLo 320 DM, a human colon adenocarcinoma line, the Jurkat leukaemia cell line and the MCF-7 breast cancer cell line. A known concentration of cells was exposed to different concentrations of complex **4** on a 96-well tissue culture plate and incubated for a period of time. Drug-free solvent controls were included. Also reported are the IC_{50} data determined under the same conditions for cisplatin, a well-established anti-cancer drug frequently used as a standard in drug performance comparisons. The viability of cells was determined by the MTT method, as described by van Rensburg *et al.*[38] Jurkat cells were the most sensitive, while the CoLo cells were the least sensitive to the carbene complex. Excluding CoLo, the derived values for the IC_{50}, representing the mean concentration (μM) of experimental compound **4**, requiring a 50% cell growth inhibition to be achieved, were considerably lower than those for cisplatin. Human lymphocytes were less sensitive to compound **4** than the cancer cells, indicating selectivity for the cancer cells. The tumour specificity was calculated as the average of the IC_{50} values for primary cultures divided by the average of the IC_{50} values for the cancer cells.

Table 4 Cytotoxicity expressed as IC_{50} values (μM)[a]

	HeLa	CoLo	Jurcat
4	0.572 ± 0.027	1.007 ± 0.081	0.253 ± 0.031
Cisplatin	0.638	0.407 ± 0.043	0.783 ± 0.054

[a] Tumour specificity of **4** = 6.976.

Conclusions

We have synthesised, in a series of steps, four new complexes containing ferrocenyl ligands, two of them NHC precursors. The gold(I)bis(carbene) complex was finally prepared by the transfer of the carbene *via* the corresponding silver(I) carbene complex, representing the first heterobimetallic gold(I) NHC complex bearing a conjugatively-attached electrophoric ferrocenyl moiety. As a result of linear gold(I)bis(carbene) formation, large differences in the dihedral angles between the planes of the NHC ligand were observed. Hydrogen bonding (C–H···F), involving the BF_4^-, counterion determines the crystal lattice organisation in **3** and **4**. The phosphine-free gold(I) complex **4** is tumor specific and achieves growth inhibition at lower concentrations than the well-known cisplatin for two of the three tested cancer cell lines. It is possible that the anti-tumour activity of the gold(I)carbene complex is enhanced by the presence of the ferrocene fragment, and this possibility should be investigated in more detail.

Experimental

Methods

Reactions were carried out under argon using standard Schlenk and vacuum line techniques. All solvents were dried according to standard literature methods under a nitrogen atmosphere.[39] Melting points were determined on a Stuart Scientific melting point apparatus SMP3 and are uncorrected. Elemental analyses were carried out by the Department of Chemistry, University of Witwatersrand, South Africa. Mass spectra were recorded on a AMD 604 high resolution mass spectrometer (EI-MS, 70 eV) or on a VG 70SEQ (FAB, 70 eV) instrument (nitrobenzyl alcohol matrices). The infrared spectra were recorded on a Nicolet Avatar 330 FT-IR with an ATR (attenuated total reflection) accessory (Smart Performer) or on a Nicolet 5700 FT-IR with an ATR diamond window. The ^1H and ^{13}C NMR spectra were recorded on a Varian 300 FT or a Varian Unity INOVA 400 MHz spectrometer (δ reported relative to the solvent resonance). Chloro(dimethylsulfide)gold(I)[40] was prepared *via* the addition of dimethylsulfide to a tetrachloroauric acid[41] solution. All the other starting materials were commercially available and were used without further purification.

1-(4-Ferrocenylphenyl)imidazole (1). A solution of sodium nitrite (0.44 g, 6.3 mmol) in H_2O (10 cm^3) was added dropwise

to an ice cold solution of 4-(1*H*-imidazol-1-yl)aniline (1.0 g, 6.3 mmol) and aqueous tetrafluoroboric acid (50%) (2.0 cm^3, 0.031 mol) in H_2O (20 cm^3), whereupon a yellowish precipitate was observed. After complete addition of the sodium nitrite solution, the mixture was stirred for another 5 min, followed by the dropwise addition of a solution of ferrocene (1.18 g, 6.3 mmol) in a mixture of CH_3CN and CH_2Cl_2 (1 : 2) (15 cm^3), resulting in a green-brown suspension. The cooling bath was removed and the mixture stirred for 1 h. Subsequently, H_2O (200 cm^3) was added and the reaction mixture extracted with CH_2Cl_2 (70 cm^3). The red organic layer was washed with a diluted Na_2CO_3 solution, causing a deepening of the red colour. After drying with Na_2SO_4, the solvent was removed *in vacuo*, resulting in a brown residue, which was washed with *n*-hexane (3 × 30 cm^3) to remove residual ferrocene. The residue was then dissolved in CH_2Cl_2 (2 cm^3) and chromatographed on a column charged with silica gel 100 (70 g), using diethyl ether as the eluent. The first yellow fraction was discarded, and the second dark orange fraction was collected and dried *in vacuo*, to yield compound **1** (0.45 g, 22%) as a red-brown, microcrystalline material.† Mp 160–162 °C. Found C, 69.26; H, 4.77; N, 8.14. $C_{19}H_{16}FeN_2$ requires C, 69.53; H, 4.91; N, 8.54%. ν_{max} (ATR)/cm^{-1}: 3118w, 3095w, 1599w, 1530s, 1508vs, 1480s, 1299s, 1257m, 1102m, 1056s, 1032m, 1004m, 962m, 900m, 838m, 808vs, 739vs, 691m, 658vs, 530s, 500s, 479s and 454s. δ_H (300 MHz, acetone-d_6): 8.08 (1H, s, H1), 7.73 (2H, m, C_6H_4), 7.58 (3H, m, C_6H_4, H4), 7.14 (1H, s, H3), 4.81 (2H, t, $J_3 = J_4 = 1.9$ Hz, η^5-C_5H_4), 4.38 (2H, t, $J_3 = J_4 = 1.9$ Hz, η^5-C_5H_4) and 4.06 (5H, s, η^5-C_5H_5). δ_C (75 MHz, acetone-d_6): 139.8 (C6), 136.5 (C7, C11), 133.8 (C1), 132.3 (C4), 129.9 (C3), 128.3 (C9), 121.9 (C8, C10), 85.1 (η^5-C_5H_4-*ipso*), 70.5 (η^5-C_5H_5) and 67.4 (η^5-C_5H_4). *m*/*z* (EI-MS): 328 (M^+, 100%), 262 (M^+ − imd [Himd = imidazole], 17%) and 207 ($M^+ - \eta^5 - C_5H_5Fe$, 12%).

1-[(*E*)-2-Butenyl]-3-(4-ferrocenylphenyl)imidazolium bromide (2). Complex **1** (0.26 g, 0.79 mmol) was reacted with 1-bromo-2-butene (85%) (0.44 cm^3, 4.3 mmol) in CH_2Cl_2 (25 cm^3). The mixture was stirred for 41 h at room temperature. After solvent removal, the mixture was treated with Et_2O (1 × 20 cm^3), filtered, washed with Et_2O (3 × 30 cm^3) and dried *in vacuo* to yield compound **2** (0.24 g, 66%) as an orange, microcrystalline material. Mp 75 °C (dec.). ν_{max} (ATR)/cm^{-1}: 3088w, 3064w, 2918w, 2856w, 1606w, 1549s, 1525m, 1435m, 1410m, 1371w, 1282w, 1198s, 1105s, 1066s, 972s, 887m, 843s, 824vs, 808s, 737s and 689s.† δ_H (400 MHz, CD_2Cl_2): 11.16 (1H, s, H1), 7.70 (4H, m, C_6H_4), 7.61 (1H, m, H4), 7.42 (1H, m, H3), 6.09 (1H, m, H13), 5.76 (1H, m, H14), 5.22 (2H, dd, $J_3 = 7.6$ Hz, $J_4 = 7.0$ Hz, H12), 4.72 (2H, t, $J_3 = J_4 = 1.9$ Hz, η^5-C_5H_4), 4.41 (2H, t, $J_3 = J_4 = 1.9$ Hz, η^5-C_5H_4), 4.06 (5H, s, η^5-C_5H_5) and 1.85 (3H, dd, $J_3 = 7.1$ Hz, $J_4 = 6.5$ Hz, H15). δ_C (101 MHz, CD_2Cl_2): 142.9 (C6), 135.9 (C7, C11), 133.9 (C1), 132.3 (C13), 127.8 (C9), 123.0 (C14), 122.2 (C4), 122.0 (C8, C10), 120.4 (C3), 82.9 (η^5-C_5H_4-*ipso*), 70.1 (m, η^5-C_5H_5), 67.1 (η^5-C_5H_4), 46.8 (C12) and 17.9 (C13). *m*/*z* (FAB): 383 (M^+ − Br, 71%), 328 (M^+ − Br − C_4H_7, 12%), 262 (M^+ − Br − imd, 5%) and 199 (M^+ − Br − Fc [Fc = ferrocene], 11%).

1-[(*E*)-2-Butenyl]-3-(4-ferrocenylphenyl)imidazolium tetrafluoroborate (3). Compound **2** (0.22 g, 0.47 mmol) was reacted with ammonium tetrafluoroborate (74 mg, 0.71 mmol) in acetone (30 cm^3). The mixture was stirred for 24 h at room temperature. After filtration through $MgSO_4$ and solvent removal, the residue was dried *in vacuo* to yield compound **3** (0.21 g, 99%) as an orange, microcrystalline material. Mp 82 °C (dec). Found C, 58.85; H, 4.81; N, 5.69. $C_{23}H_{23}BF_4FeN_2$ requires 58.76; H, 4.93; N, 5.96%. ν_{max} (ATR)/cm^{-1}: 3171w, 3111vw, 2941vw, 1556m, 1531w, 1454w, 1105m, 1092m, 1049vs, 1030vs, 1011s, 982s, 887m, 825s, 811s, 734m and 690m.† δ_H (400 MHz, CD_2Cl_2): 9.21 (1H, s, H1), 7.67 (2H, d, J_3 8.2 Hz, H8, H10), 7.62 (1H, bs, H4), 7.52 (2H, m, H7, H11), 7.47 (1H, m, H3), 6.10 (1H, m, H13), 5.75 (1H, m, H14), 4.96 (2H, dd, $J_3 = 7.3$ Hz, $J_4 = 6.7$ Hz, H12), 4.73 (2H, m, η^5-C_5H_4), 4.42 (2H, m, η^5-C_5H_4), 4.07 (5H, s, η^5-C_5H_5) and 1.84 (3H, m, H15). δ_C (101 MHz, CD_2Cl_2): 143.3 (C6), 136.5 (C7, C11), 134.3 (C1), 132.1 (C13), 127.8 (C9), 122.9 (C14), 122.5 (C4), 122.4 (C8, C10), 121.7 (C3), 82.9 (C_5H_4-*ipso*), 70.3 (η^5-C_5H_5), 67.2 (η^5-C_5H_4), 49.7 (C12) and 17.9 (C15). *m*/*z* (FAB): 383 (M^+ − BF_4, 80%), 328 (M^+ − BF_4 − C_4H_7, 15%), 262 (M^+ − BF_4 − imd, 8%) and 199 (M^+ − BF_4 − Fc, 19%).

Bis{1-[(*E*)-2-butenyl]-3-(4-ferrocenylphenyl)-2*H*-imidazol-2-ylidene}gold(I) tetrafluoroborate (4). Complex **3** (0.11 g, 0.24 mmol), tetraethylammonium chloride (40 mg, 0.24 mmol) and Ag_2O (61 mg, 0.26 mmol) were reacted in a mixture of CH_2Cl_2 and MeOH (1 : 1) (30 cm^3). The mixture was stirred for 5 h at room temperature, followed by the addition of chloro(dimethylsulfide)gold(I) (42 mg, 0.14 mmol) and further stirring for 4 h at room temperature. After filtration through Celite and solvent removal, the residue was treated with CH_2Cl_2 (20 cm^3), and the extract filtered through $MgSO_4$/Celite. The solution was reduced to dryness *in vacuo* yielding complex **4** (0.17 g, 68%) as an orange, microcrystalline material. Mp 58–65 °C (dec). Found C, 52.54; H, 4.33; N, 5.23. $C_{46}H_{44}AuBF_4Fe_2N_4$ requires C, 52.70; H, 4.23; N, 5.34%. ν_{max} (ATR)/cm^{-1}: 3136vw, 2964vw, 1527m, 1458w, 1423w, 1410w, 1259w, 1188w, 1095m, 1080s, 1047vs, 1030vs, 968m, 887m, 818s, 798s, 743m and 694m.† δ_H (400 MHz; CD_2Cl_2): 7.54 (4H, m, H8, H10), 7.47 (4H, m, H7, H11), 7.34 (2H, m, $J_3 = 1.9$ Hz, H4), 7.22 (2H, m, $J_3 = 1.9$ Hz, H3), 5.80 (2H, m, H13), 5.63 (2H, m, H14), 4.77 (4H, m, H12), 4.69 (4H, m, η^5-C_5H_4), 4.43 (4H, m, η^5-C_5H_4), 4.06 (10H, s, η^5-C_5H_5) and 1.74 (6H, m, H15). δ_C(101 MHz, CD_2Cl_2): 182.5 (C═Au), 141.7 (C6), 136.9 (C7, C11), 132.8 (C13), 127.0 (C9), 125.1 (C8, C10), 125.0 (C14), 122.7 (C4), 121.9 (C3), 83.4 (C_5H_4-*ipso*), 70.1 (η^5-C_5H_5), 67.1 (η^5-C_5H_4), 48.3 (C12) and 17.9 (C15). *m*/*z* (FAB): 961 (M^+ − BF_4, 18%) and 777 (M^+ − BF_4 − Fc, 5%).

Crystal structure determination

Single crystals of **1** suitable for X-ray analysis, were obtained by slow evaporation from a CH_2Cl_2 solution at room temperature, and for **3** and **4** by slow crystallisation from CH_2Cl_2 solutions layered with *n*-hexane at −20 °C. Data and parameters of the crystal structure determinations are shown in Table 5.‡ For compound **1**, a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) and a nominal crystal to area detector

Table 5 Crystal data and structure refinements for **1**, **3** and **4**

Compound	**1**	**3**	**4**
Empirical formula	$C_{19}H_{16}FeN_2$	$C_{23}H_{23}BF_4FeN_2$	$C_{48}H_{48}AuBCl_4F_4Fe_2N_4$
Formula weight	328.19	470.09	703.42
Crystal habit	Prism	Cubes	Prism
Crystal colour	Orange	Red	Orange
Crystal size/mm	0.35 × 0.2 × 0.2	0.25 × 0.23 × 0.20	0.20 × 0.20 × 0.15
Crystal system	Monoclinic	Monoclinic	Trigonal
Space group	$P2_1/c$	$P2_1/n$	R-3
a/Å	15.0730(4)	9.891(2)	22.070(2)
b/Å	7.7163(2)	18.733(3)	22.070(2)
c/Å	12.8686(2)	11.461(2)	25.746(6)
α/°	90	90	90
β/°	104.784(2)	99.699(3)	90
γ/°	90	90	120
V/Å^3	1447.17(6)	2093.3(6)	10 860(2)
Z	4	4	9
D_{calc}/mg cm^{-3}	1.506	1.492	1.676
Adsorption coefficient/mm^{-1}	1.039	0.768	3.900
F(000)	680	968	5436
θ (min − max)/°	2.80–26.00	2.11–25.68	2.93–25.69
Index ranges, hkl	−18–0, −9–9, −15–15	−12–10, −19–22, −13–11	−23–26, −23–26, −28–31
Temperature/K	233(2)	100(2)	100(2)
Reflections collected	9126	11 371	16 730
Independent reflections	2837 [R_{int} = 0.0182]	3958 [R_{int} = 0.0505]	4472 [R_{int} = 0.0654]
Data/restraints/parameters	2837/0/199	3958/0/281	4472/0/298
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0234, wR_2 = 0.0627	R_1 = 0.0494, wR_2 = 0.1075	R_1 = 0.0521, wR_2 = 0.1261
R indices (all data)[a]	R_1 = 0.0263, wR_2 = 0.0646	R_1 = 0.0790, wR_2 = 0.1193	R_1 = 0.0929, wR_2 = 0.1411
Goodness-of-fit on F^2	1.033	1.039	0.922
Largest peak/e Å^{-3}	0.222	0.534	2.508
CCDC number	668306	668307	668308

[a] The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$, with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c)/3$.

distance of 36 mm was used. Intensities were integrated using DENZO and scaled with SCALEPACK.[42] Several scans in φ and ω directions were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces, in a good approximation, an empirical absorption correction. For compounds **3** and **4**, a Bruker SMART Apex diffractometer[43–46] with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) was used for data collection. Intensities were measured using the ω-scan mode and corrected for Lorentz and polarisation effects. All structures were solved by direct methods (**1** and **4**) or Patterson synthesis (**3**) and refined by full matrix least-squares on F^2 using the SHELXL-97 program package and X-Seed.[47–50] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined using a riding model. Figures were created using POV-RAY 3.5.

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