Reactions of $[Au(C_6F_5)(SC_4H_8)]$ with diazoalkanes. Synthesis and molecular structures of $[Au(C_6F_5)(Ph_2C=N-N=CPh_2)]$

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Abstract

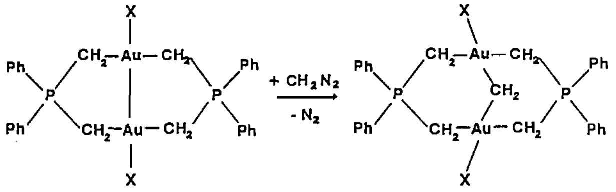
Treatment of $[Au(C_6F_5)(SC_4H_8)]$ (1) (SC_4H_8 = tetrahydrothiophene, tht) with Ph_2CN_2 affords the azine complex $[Au(C_6F_5)(Ph_2C=N-N=CPh_2)]$ (2), whereas $HAuCl_4$ reacts with diphenyldiazomethane to form the salt $[Ph_2C=N(H)-N=CPh_2][AuCl_4]$ (3). The molecular structures of both 2 and 3 have been established by single crystal X-ray diffraction studies. Complex 2 (triclinic, $P\bar{1}$, $Z=2$, $a=10.805(4)$, $b=13.066(2)$, $c=10.094(3)$ Å, $\alpha=112.06(3)$, $\beta=100.63(2)$, $\gamma=88.45(2)$°) exhibits the expected linear coordination with the azine acting as N-monodentate ligand. Bond parameters of interest are Au–C(perfluorophenyl) 1.992(6), Au–N(azine) 2.069(5) Å, C–Au–N 175.8(2)°. 3 (triclinic, $P\bar{1}$, $Z=1$, $a=9.145(5)$, $b=9.333(1)$, $c=8.228(3)$ Å, $\alpha=100.08(1)$, $\beta=107.30(3)$, $\gamma=74.17(2)$°) is an ionic species in which the cation is the monoprotonated derivative of the azine coordinated to gold in 2. Bond parameters within the azine molecule in the two derivatives are comparable. Complex **1** promotes dinitrogen elimination from diazofluorene to form fluoren-9-ylidene via carbene–carbene coupling. An interpretation of the different behaviour of the two diazocompounds is presented.

Key words: Crystal structures; Gold complexes; Diazoalkane complexes; Azine complexes

Introduction

Diazocompounds, R_2CN_2, can react with a variety of metal complexes either as a source of the carbene fragment: CR_2 or, without loss of molecular nitrogen, as N-donor ligands. In the case of gold complexes only two types of reactions are presently known: insertion of a carbene moiety into an Au(I)–X bond (X = halogen) [1] and oxidative addition to dinuclear Au(II) ylide complexes to give methylene bridged species [2] (Scheme 1).

$$[AuCl(PPh_3)] + CH_2N_2 \longrightarrow [Au(CH_2Cl)(PPh_3)] + N_2$$



Scheme 1.

Since neither carbene complexes of the type $L_nAu=CR_2$ nor diazocomplexes have been reported for this metal, we have initiated a study on the reactivity of gold complexes toward diazoalkanes. The complex $[Au(C_6F_5)(SC_4H_8)]$ (1) (SC_4H_8 = tetrahydrothiophene) seemed the ideal starting material for the following reasons: (i) it contains the labile SC_4H_8 ligand and (ii) the $M–C_6F_5$ bond is usually reluctant to undergo insertion reactions.

In this paper we report the reaction of 1 with Ph_2CN_2 that affords $[Au(C_6F_5)(Ph_2C=N-N=CPh_2)]$ (2) which is, to the best of our knowledge, the first example of a gold diazo complex, according to the broad definition given by Sutton [3], and the characterization of the new species by means of an X-ray diffraction study.

The mechanism of this reaction is presented and compared with the results of the reaction of 1 with diazofluorene which catalytically affords fluoren-9-ylidene.

Results and discussion

The room temperature reaction of $[Au(C_6F_5)(SC_4H_8)]$ (1) with a double molar ratio of diphenyldiazomethane

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in diethyl ether leads to the formation of the ketazine complex $[\overline{\mathrm{Au}(C_6F_5)(Ph_2C{=}\mathrm{N}}{-}N{=}CPh_2)]$ (**2**) which has been obtained as a white crystalline solid (*c.* 70% yield).

$$[\mathrm{Au}(C_6F_5)(SC_4H_8)] + 2Ph_2CN_2 \longrightarrow$$
$$\mathbf{1}$$
$$[\overline{\mathrm{Au}(C_6F_5)(Ph_2C{=}\mathrm{N}}{-}N{=}CPh_2)] + SC_4H_8 + N_2 \quad (1)$$
$$\mathbf{2}$$

The nature of complex **2** has been established by elemental analysis and spectroscopic data. Its ^1H NMR spectrum shows only resonances in the aromatic region, whereas the IR spectrum displays the expected $\nu(C_6F_5)$ absorptions (1503, 1447, 1049, 946 cm^{-1}). There is IR activity in the range 1500–1600 cm^{-1} and specific assignment is not possible; however a weak band at 1556 cm^{-1} can be assigned to the C=N stretching of the coordinated benzophenoneazine ligand [4]. The latter band is slightly shifted to lower wavenumbers (about 10 cm^{-1}) with respect to the free ligand. Finally, the FAB-MS spectrum shows the parent ion at 724 *m/e* (M^+) together with the peaks due to the loss of C_6F_5 (557) and the azine ligand (360).

Complex **2** decomposes within 24 h at room temperature to a black solid, but remains unchanged for several months when stored at −20 °C under nitrogen. It is soluble in Et_2O, THF and insoluble in hexane. In chlorinated solvents or in MeCN it slowly decomposes to metallic gold with concomitant loss of the azine ligand which has been identified both by ^{13}C and ^1H NMR spectra. Further evidence of the lability of the coordinated benzophenone azine has been obtained from the reaction of **2** with 2,6-dimethylphenylisocyanide (CNXy) in refluxing THF which readily occurs with the displacement of the ligand and the formation of $[\mathrm{Au}(C_6F_5)(CNXy)]$. After separation, the nature of this latter complex has been established by the IR spectrum which shows an absorption at 2214 cm^{-1}, attributable to ν(CN) of the coordinated isocyanide, in accordance with the value reported in the literature for the analogous $[\mathrm{Au}(C_6F_5)(CNPh)]$ [5].

The X-ray molecular structure of compound **2** is shown in Fig. 1 and relevant bond distances and angles are listed in Table 1. The gold atom exhibits the expected linear two-coordination typical for the d^{10} M^+ ions (C(3)–Au–N(1) 175.8(2)°). The Au–C distance, 1.992(6) Å, is strictly comparable to the value found in $[(C_6F_5)AuCH(Ph_2PAuPPh_2)_2CHAu(C_6F_5)]$, 2.01(1) Å [6], and shorter than the Au–C(aryl) 'standard' bond of 2.053(9) Å [7]. The C_6F_5 ligand exhibits distortions from the sp^2 values for the *ipso* and *ortho* endocyclic angles (114.3(5), 123.2(6) and 123.0(6)°, respectively), as already observed in the aforementioned complex $[(C_6F_5)AuCH(Ph_2PAuPPh_2)_2CHAu(C_6F_5)]$ and in general in mono-substituted benzene rings [8]. The C(8)–C(3)–Au angle is also distorted (123.9(5)° in **2** versus 126.5(7)° in $[(C_6F_5)AuCH(Ph_2PAuPPh_2)_2$-$CHAu(C_6F_5)])$. The Au–C distance can be explained only in part in terms of shrinkage of the carbon orbitals

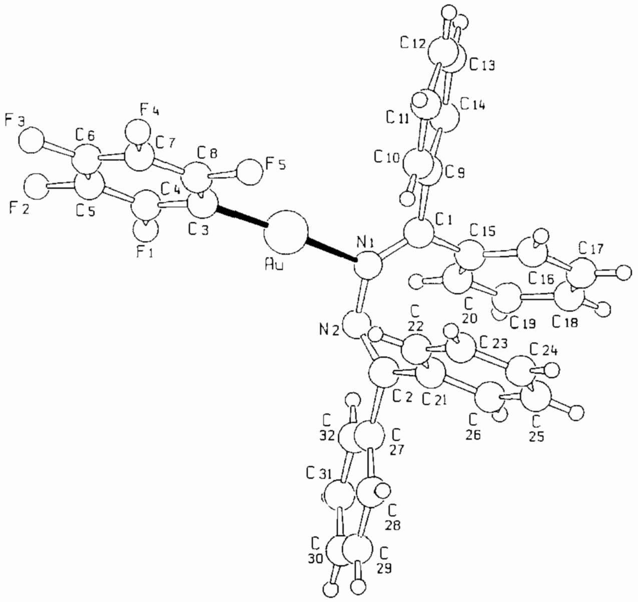


Fig. 1. The molecular structure of **2** showing the atomic labelling. Hydrogen atoms bear the same labelling as the corresponding C atoms.

TABLE 1. Selected bond distances (Å) and angles (°) for **2** and **3**

	2		**3**
Au–N(1)	2.069(5)		
Au–C(3)	1.992(6)		
N(1)–N(2)	1.408(7)	N(1)–N(1′)	1.376(5)
N(1)–C(1)	1.291(7)	N(1)–C(1)	1.301(3)
N(2)–C(2)	1.288(7)		
C(1)–C(9)	1.476(8)	C(1)–C(2)	1.471(4)
C(1)–C(15)	1.489(7)	C(1)–C(8)	1.482(4)
C(2)–C(21)	1.486(8)		
C(2)–C(27)	1.495(8)		
C–F av.	1.354(7)		
$C(C_6F_5)$–$C(C_6F_5)$	1.36(1) av.		
Au...F(1)	3.135(4)	Au–Cl(1)	2.276(1)
Au...F(5)	3.204(4)	Au–Cl(2)	2.277(1)
C(3)–Au–N(1)	175.8(2)	Cl(2)–Au–Cl(1)	90.08(3)
Au–N(1)–C(1)	126.9(4)		
Au–N(2)–C(2)	110.4(3)		
N(2)–N(1)–C(1)	121.3(5)	N(1′)–N(1)–C(1)	118.7(3)
N(1)–N(2)–C(2)	117.6(5)	N(1)–C(1)–C(2)	117.0(3)
Au–C(3)–C(4)	121.8(5)		
Au–C(3)–C(8)	123.9(5)		
C(4)–C(3)–C(8)	114.3(5)		
C(3)–C(4)–C(5)	123.2(6)		
C(4)–C(5)–C(6)	119.6(6)		
C(5)–C(6)–C(7)	119.3(6)		
C(6)–C(7)–C(8)	120.5(6)		
C(3)–C(8)–C(7)	123.0(6)		

induced by the electronegative F atoms, because the average C–C distance in the perfluorophenyl ring (1.36(1) Å) is only 0.03 Å shorter than in the coordinated C_6H_5 rings (av. 1.39 Å). There is, in addition to the $[(C_6F_5)AuCH(Ph_2PAuPPh_2)_2CHAu(C_6F_5)]$ species, another report of the Au–C(C_6F_5) distance in the complex $[Au(C_6F_5)(PPh_3)]$ [9], where the value is significantly longer (2.07(2) Å). These figures cannot be explained in terms of σ bonds only. Some π gold-to-perfluorophenyl bond should be invoked in order to rationalize strictly comparable values when the *trans* ligands do not act as π acceptors (the *trans* ligand in $[(C_6F_5)AuCH(Ph_2PAuPPh_2)_2CHAu(C_6F_5)]$ binds through an sp^3 methanide carbon atom). The longer value in $[Au(C_6F_5)(PPh_3)]$ can be viewed as the result of the competition in π bonding of the phosphine ligand.

The azine ligand acts as monodentate σ donor (Au–N(1) 2.069(5) Å), in spite of the unsaturation of the metal centre and the ability of the azine ligands to act as bidentate, as found in *cis*-$[V(C_5Me_5)(CO)_2(PhHC{=}NN{=}CHPh)]$ [10]. The azine adopts a skewed conformation around the N-N single bond (N(1)–N(2) 1.408(7) Å, C(1)–N(1)–N(2)–C(2) torsion angle 81.3(6)°). In this way, the lone pair of N(2) points away from the gold atom and one can infer that the electronic requirements of the metal atom are sufficiently saturated by N(1) and C(3). The C_6F_5Au moiety forms a dihedral angle of 53.0(6)° with the C(1)=N(1)–N(2) system; this value is probably the result of packing optimization. The differences in bond parameters at the coordinated N(1) and free N(2) are small (N(1)–C(1) 1.291(7), N(2)–C(2) 1.288(7) Å, N(2)–N(1)–C(1) 121.3(5)°, N(1)–N(2)–C(2) 117.6(5)°). Of some significance is the asymmetry in bond angles, reflecting the different hindrances of the lone electron pair at N(2) and the bonded pair at N(1). It should be noted that the Au–N(1)–C(1) and Au–N(1)–N(2) angles are significantly different (126.9(4) versus 110.4(3)°, respectively). This effect can be attributed to the asymmetry of the non-bonded interactions among the electrons in the Au–N(1) bond and those in the N(1)–C(1) double bond and N(1)–N(2) single bond. Another hypothesis is that this angular distortion is induced by some Au...N(2) attraction (contact 2.881(5) Å, shorter than the sum of the van der Waals radii, 3.2 Å). That the latter is not the case is demonstrated by the very similar structural features found in $[PdCl_2(PhCH{=}N{-}N{=}CHPh)_2]$ [11] and $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(Me_2C{=}N{-}N{=}CMe_2)]$ [12], where the metal atoms are richer both in electrons and ligands and certainly do not require further interactions. The Au...Au shortest contacts in the crystal packing are not less than 6 Å, due to the sterical encumbrance of the ligands; thus no intermetallic interactions are observed of the kind frequently reported and recently reviewed on a statistical basis on a variety of bicoordinate gold(I) derivatives [13].

Complex **2** has also been obtained by reacting **1** in refluxing THF for 3 h with the stoichiometric amount of the preformed azine ligand. This latter reaction, carried out under the same experimental conditions as eqn. (1), takes several days to go to completion revealing a catalytic role of the gold complex **1** in the diphenyl diazomethane dimerization to ketazine. Therefore the formation of complex **2** is in agreement with the previously observed ability of Group 10 metals to form compounds in which the azine ligands arising from diazoalkane coupling are coordinated either in a (C,N-η^2) as in $[M\{C(CF_3)_2N{-}N{=}C(CF_3)_2\}L_2]$ (M = Ni, Pd or Pt) [14] or through one N atom and the π system of a phenyl group as in $[Pt(C_6F_5)\{(2\text{-}C_6H_4)C(Ph{=}N{-}N(\eta^2\text{-}C_6H_5)CPh\}]$ [15].

The stability of complex **2** is attributable to the presence of the C_6F_5 ligand. In fact, both [AuCl(tht)] and $[AuPPh_3]BF_4$ produce the free azine upon reaction with Ph_2CN_2. Even at low temperature the Ph_2CN_2 adducts cannot be isolated from the reaction mixtures. It has been observed that the azine formation is faster for the $[AuPPh_3]^+$ complex than in the case of [AuCl(tht)]. This may be attributed to the higher acidity of the metal centre. In this respect it should be mentioned that $[HAuCl_4]$ reacts with diphenyl diazomethane to form the tetrachloroaurate salt $[Ph_2C{=}N(H)N{=}CPh_2][AuCl_4]$ (**3**), which has also been characterized by an X-ray diffraction study.

The cation of **3**, shown in Fig. 2, is the monoprotonated derivative of the azine molecule coordinated to gold in **2**. It is placed across an inversion centre in the

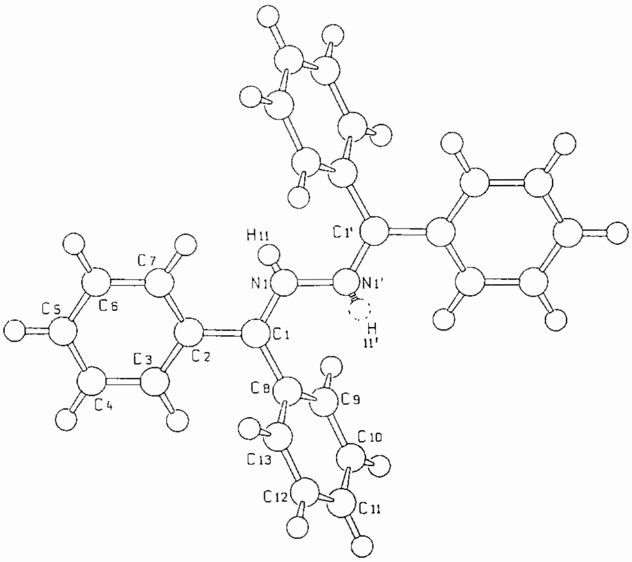
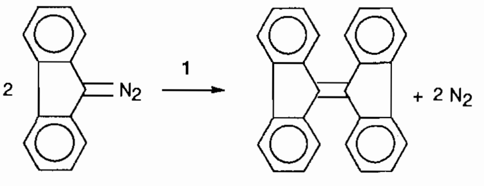


Fig. 2. The molecular structure of **3** showing the labelling of the independent atoms. Phenyl hydrogen atoms bear the same labelling as the corresponding C atoms.

crystal and the C=N–N=C chain is forced to adopt the *trans* planar conformation. The proton is statistically distributed over the two nitrogen atoms and a discussion of the differences between the protonated and unprotonated nitrogen atom is not possible. The disorder also hinders an accurate comparison between the molecule coordinated to H^+ and Au^+, apart from the conformational changes. The averaged bond parameters (C=N 1.301(3), N-N 1.376(5) Å, C=N–N 118.7(3)°) are similar, within the standard deviations, to the average values found in the coordinated molecule just described. It is worth mentioning that the structures of benzalazine and its ordered monoprotonated derivative [16] show small changes in bond parameters and the effects of protonation are interestingly similar to those of auration discussed above. The counterion, $[AuCl_4]^-$, sits on a crystallographic inversion centre and the bond parameters are very similar to those reported in the numerous determinations of its structure [17].

Proposals for the formation of complex **2** or free azine remain necessarily speculative; however, in the light of previously reported observations on the interaction between diazoalkanes and metal centres, it is reasonable to suppose a gold carbene as an unstable intermediate (A) which undergoes diazoalkane N-addition at the carbene carbon atom to form (B) and then complex **2** through an intramolecular rearrangement, as depicted in the left-hand side of Scheme 2.

The depicted reaction pathway does not account for the observed catalytic transformation of the diazofluorene into the fluoren-9-ylidene in the presence of $[Au(C_6F_5)(tht)]$. This latter reaction occurs in petroleum ether at room temperature, with a 3:1 molar ratio between the diazofluorene and **1**.



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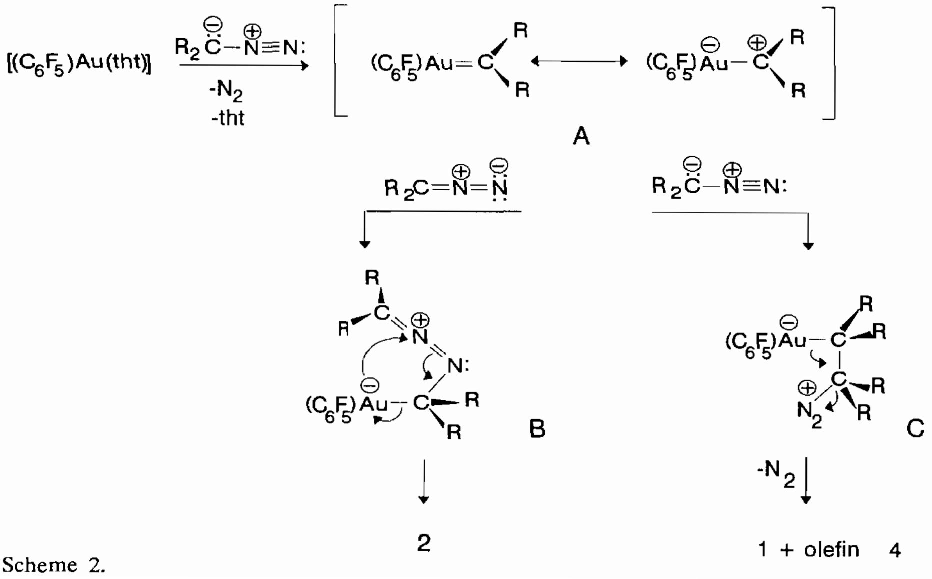
The formation of the olefin rather than the azine may be attributed to the nature of the diazoalkane. The higher wavenumber absorption of the $\nu(CN_2)$ in the diazofluorene (2058 cm^{-1}) compared with the diphenyldiazomethane (2041 cm^{-1}) is indicative of a major contribution of the $R_2\bar{C}-\overset{+}{N}\equiv N$ resonance structure in the former case. Therefore it is reasonable to suppose a nucleophilic addition of the diazofluorene on the carbon atom of A (Scheme 2) to form a C–C bond in the intermediate C which produces the olefin restoring complex **1**. The formation of the free olefin can be explained by the reluctance of the $Au(C_6F_5)$ fragment to form π-bonded species [18], probably because of the π Au–C_6F_5 interaction discussed above.

Experimental

General procedures

All reactions were carried out under a dinitrogen atmosphere using standard Schlenk technique. The solvents were dried and freshly distilled before use; petroleum ether refers to the b.p. 40–60 °C fraction. IR spectra were recorded over the range 4000–180 cm^{-1} using KBr disks with a Perkin-Elmer 983-G spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer with $SiMe_4$ as



Scheme 2.

internal standard. Elemental analyses were determined by Pascher Microanalytical Laboratorium (Remagen, Germany). All FAB-MS spectra were recorded with a VG 7070EQ instrument in a matrix of nitrobenzyl alcohol. Literature methods were used to prepare $[Au(C_6F_5)(SC_4H_8)]$ (**1**) [19], Ph_2CN_2 [20], $Ph_2C{=}N{-}N{=}CPh_2$ [21] and $C_{12}H_8CN_2$ (diazofluorene) [22].

Preparation of $[Au(C_6F_5)(Ph_2C{=}N{-}N{=}CPh_2)]$ *(2)*

(a) From Ph_2CN_2

By adding Ph_2CN_2 (0.36 g, 1.86 mmol) to a solution of **1** (0.42 g, 0.93 mmol) in diethyl ether (20 ml) a slow gas evolution was observed. After 3 h at room temperature the solution became pale yellow. After filtration through celite the solvent was evaporated to dryness and the resulting residue was washed twice with petroleum ether. The white residue was crystallized from Et_2O/petroleum ether at 4 °C to give complex **2** as a white crystalline solid (0.47 g, 70%). *Anal.* Found: C, 53.62; H, 3.34; N, 3.80. Calc. for $C_{32}H_{20}AuF_5N_2$: C, 53.05; H, 2.78; N, 3.87%. This route provided the crystal which was analyzed by X-rays.

(b) From $Ph_2C{=}N{-}N{=}CPh_2$

A THF solution (30 ml) containing equimolar quantities of **1** (0.32 g, 0.71 mmol) and $Ph_2C{=}N{-}N{=}CPh_2$ (0.25 g, 0.71 mmol) was refluxed for 3 h. By workup of the resulting pale yellow solution as in the previous section, 0.31 g (61%) of **2** were obtained.

Preparation of $[Ph_2C{=}N(H){-}N{=}CPh_2][AuCl_4]$ *(3)*

To a stirred suspension of $HAuCl_4$ (0.30 g, 0.76 mmol) in petroleum ether (25 ml) was slowly added an excess of Ph_2CN_2 (0.59 g, 3.04 mmol). After 3 h at room temperature a green–yellow solid was formed and after filtration it was crystallized from CH_2Cl_2/petroleum ether at 4 °C to give yellow crystals (0.29 g, 51%). FAB(−)-MS (*m/e*): 337, 339, 341, 343, 345 ($AuCl_4^-$); FAB(+)-MS (*m/e*): 361 ($Ph_2C{=}N(H){-}N{=}CPh_2$). ^1H NMR (acetone): $\delta = 7$–8 (20H, aromatics). ^{13}C NMR (acetone): $\delta = 175.0$ (*C*=N), 130–140 (*C*, aromatics). IR (cm^{-1}, KBr): $\nu = 3231$w (NH); 1547m (C=N); 355m (AuCl). M.p. (°C) 188(d). *Anal.* Found: C, 45.10; H, 3.41; N, 4.02. Calc. for $C_{26}H_{21}AuCl_4$: C, 44.60; H, 3.02; N, 4.00%.

Reaction of 1 with diazofluorene

A suspension of **1** (0.14 g, 0.31 mmol) in 30 ml of light petroleum either (b.p. 30–40 °C) was cooled to −20 °C. Diazofluorene (0.18 g, 0.92 mmol) was added dropwise and after addition was complete the mixture was allowed to warm to room temperature. After stirring for 4 h the colour of the suspension changed from red to dark orange and all the starting diazofluorene was transformed into the corresponding alkene that can be separated from the gold complex **1** by chromatography on a silica gel column (2×10 cm) with a mixture of light petroleum–diethyl ether (2:1) as eluent (0.14 g, 90%). Fluoren-9-ylidene: m.p. (°C) 186; MS (*m/e*): 328(M+). ^1H NMR (CD_2Cl_2): $\delta = 7.16$ (8H, m), 7.62 (4H, m), 8.26 (4H, m). ^{13}C NMR (CD_2Cl_2): $\delta = 142.8$, 141.8, 139.4 (1*C*, q), 130.4, 128.0, 127.8, 121.0 (1*C*H, aromatics).

X-ray structural determination

Crystal data and details of measurements are summarized in Table 2. Diffraction intensities for both species were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares (based on F^2 and F for **2** and **3**, respectively) using the SHELXS86 and SHELXL93 systems of programs [23]. Absorption correction was applied by azimuthal scan of some reflections. All non-hydrogen atoms were allowed to vibrate anisotropically. The H atoms were added in calculated positions (C–H 0.93 Å for the aromatic ones), apart from the H bound to N atom in **3**, which was experimentally located on

TABLE 2. Crystal data and details of measurements for **2** and **3**

	2	**3**
Formula	$C_{32}H_{20}AuF_5N_2$	$C_{26}H_{21}AuCl_4N_2$
Molecular weight	724.5	641.7
Temperature	293	293
System	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.805(4)	9.145(5)
b (Å)	13.066(2)	9.333(1)
c (Å)	10.094(3)	8.228(3)
α (°)	112.06(3)	100.08(1)
β (°)	100.63(2)	107.30(3)
γ (°)	88.45(2)	74.17(2)
V (Å^3)	1296.7(7)	641.7(6)
Z	2	1
$F(000)$	700	338
λ (Mo Kα) (Å)	0.71069	0.71069
μ (Mo Kα) (mm^{-1})	57.1	61.7
θ range (°)	2–25	2–28
ω-Scan width (°)	0.8	0.9
Requested counting $\sigma(I)/I$	0.02	0.02
Prescan rate (° min^{-1})	4	8
Prescan acceptance	0.5	0.5
Maximum scan time	40	80
Octants explored	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$
Measured reflections	4763	2753
Unique reflections used in refinement	4344	2566
No. refined parameters	361	154
GOF on F^2	1.02	1.13
R^1 (on F, $I > 2\sigma(I)$)	0.031	0.018
R^2_w (on F^2, all data)	0.075	0.047

TABLE 3. Atomic coordinates ($\times 10^4$) for **2**

	x	*y*	*z*
Au	4153(1)	2215(1)	4615(1)
N(1)	5790(4)	1983(4)	5882(5)
N(2)	5768(4)	2554(4)	7369(5)
F(1)	1382(4)	2016(4)	5044(5)
F(2)	−841(4)	2230(4)	3520(5)
F(3)	−942(4)	2818(4)	1203(5)
F(4)	1212(5)	3095(4)	343(5)
F(5)	3432(4)	2865(4)	1815(5)
C(1)	6618(5)	1260(5)	5460(6)
C(2)	6544(5)	3394(5)	8076(6)
C(3)	2509(6)	2426(5)	3499(7)
C(4)	1390(6)	2292(6)	3874(7)
C(5)	235(6)	2406(6)	3106(8)
C(6)	181(6)	2672(6)	1921(8)
C(7)	1249(7)	2813(6)	1515(7)
C(8)	2391(6)	2697(5)	2289(7)
C(9)	6570(5)	681(5)	3883(6)
C(10)	6475(6)	1268(5)	2989(7)
C(11)	6432(7)	716(7)	1514(7)
C(12)	6473(6)	−422(6)	931(8)
C(13)	6554(6)	−1009(6)	1809(7)
C(14)	6624(6)	−456(5)	3291(7)
C(15)	7634(5)	989(5)	6475(6)
C(16)	8859(6)	989(6)	6232(8)
C(17)	9825(6)	755(7)	7158(8)
C(18)	9585(8)	500(6)	8277(8)
C(19)	8377(7)	486(6)	8499(8)
C(20)	7396(6)	739(5)	7618(7)
C(21)	7524(5)	3791(5)	7503(6)
C(22)	7244(6)	4112(5)	6327(7)
C(23)	8187(8)	4446(6)	5810(8)
C(24)	9414(8)	4478(7)	6475(9)
C(25)	9702(6)	4188(7)	7649(8)
C(26)	8753(6)	3845(6)	8172(7)
C(27)	6467(5)	3973(5)	9647(6)
C(28)	6802(6)	5096(5)	10349(7)
C(29)	6710(6)	5636(6)	11784(8)
C(30)	6308(6)	5074(6)	12531(7)
C(31)	5994(7)	3962(6)	11857(7)
C(32)	6069(6)	3413(5)	10416(7)

a difference Fourier map (N–H 0.86 Å). This hydrogen is present at 50% in occupancy on both the nitrogen atoms, owing to the crystallographic inversion centre lying halfway through the N–N bond. The isotropic temperature factors for the aromatic hydrogen atoms were fixed to be 1.2 times the equivalent isotropic thermal factors of the parent C atoms, while for the N-bound hydrogen the temperature factor converged to 0.04(1) Å^2. The final ΔF maps contained peaks not exceeding 0.7 e Å^{-3} in **2** and 0.3 e Å^{-3} in **3**. The peaks were located in the proximity of the Au atom.

Fractional atomic coordinates for **2** and **3** are listed in Tables 3 and 4, respectively.

TABLE 4. Atomic coordinates ($\times 10^4$) for **3**

	x	*y*	*z*
Au	5000	0	5000
Cl(1)	6926(1)	−44(1)	7506(1)
Cl(2)	3719(1)	2318(1)	5908(1)
N(1)	212(3)	4907(3)	4246(3)
C(1)	1183(3)	5653(3)	4130(3)
C(2)	1723(3)	5318(3)	2559(3)
C(3)	2313(4)	6365(4)	2087(4)
C(4)	2815(5)	6079(5)	604(4)
C(5)	2738(4)	4738(4)	−411(4)
C(6)	2150(4)	3699(4)	47(4)
C(7)	1649(4)	3970(3)	1520(4)
C(8)	1715(3)	6817(3)	5479(3)
C(9)	636(4)	8023(4)	6027(5)
C(10)	1163(5)	9143(4)	7219(6)
C(11)	2766(5)	9042(4)	7880(5)
C(12)	3831(4)	7844(5)	7363(4)
C(13)	3325(3)	6731(4)	6158(4)

Supplementary material

Additional material available from the Cambridge Crystallographic Data Centre comprises complete listings of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and structure factor tables.

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