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Synthesis and molecular structures of the cationic gold(I)–aziridine complexes $[Ph_3PAuAz]O_3SCF_3$ (Az = C_2H_4NH, $CH_2CHMeNH$, CH_2CMe_2NH, $CH_2CHEtNH$, $CH_2CHPhNH$, C_2H_4NBz, $C_2H_4NC_2H_4OH$)

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Abstract

The gold(I) complex Ph_3PAuCl (**1**) reacts in the presence of AgO_3SCF_3 (=AgOTf) with a series of aziridines with various NH-, NR-, CHR- and CR_2-functionalities via halide elimination at ambient temperature, to give the cationic mixed phosphane-aziridine gold(I) complexes $[Ph_3PAuAz]OTf$ (**2**–**8**) (Az = aziridine, 2-methylaziridine, 2,2-dimethylaziridine, 2-ethylaziridine 2-phenylaziridine, *N*-benzylaziridine, *N*-hydroxyethylaziridine). The X-ray structure analyses show the gold(I) centres are linearly coordinated by the PPh_3 and Az ligands, and the intact three membered aziridine rings coordinate through the distorted tetrahedral N-atoms. Compounds **2**–**8** are stable with respect to both directed thermal or photolytic alkene elimination, or any ring N–C opening reaction which would result in the corresponding cationic nitrene complexes $[Ph_3PAuNH]OTf$ and $[Ph_3PAuNR]OTf$, or any oxidative addition products. The phenyl substituent in the 2-position of **6** is obviously bowed with its plane towards the Au centre, indicating some Au–π-ring interaction with the distance Au–$C_n \approx 4.00$ Å. The O atom of the hydroxy group in **8** also lies very close to the Au centre, with the distance Au–O = 3.078 Å. The IR, ^1H, ^{13}C and ^{31}P NMR, and MS spectra are reported and discussed, and the molecular structures of **3**, **4**, **6** and **8** have been determined by single crystal X-ray diffraction analyses.

Keywords: Gold(I) complexes; Aziridine ligands; Au–π-ring interaction; X-ray crystalography

1. Introduction

Although aziridines are isolobal to oxiranes and thiiranes (C_2H_4X; X = NH, O, S), their reactivity as ligands in transition metal complexes is quite different. Oxiranes and thiiranes are suitable oxidation (and oxidative addition) reagents for organic compounds, and are also useful in organometallic chemistry for the synthesis of oxo (and acylmethyl) and thio complexes by simple and easy alkene elimination [1,2]. It is interesting to note, only few examples of C_2H_4X complexes (X = O, S) are known. The aziridines, however, generally remain intact as three-membered rings, and coordinate through their N atom when reacted with transition metal complexes [3–9]. Hitherto, no nitrene complex has been generated by the alkene elimination of an aziridine. In two papers, however, a N–C ring opening reaction of aziridine ligands with hydrido- and chloro complexes $CpMo(CO)_3X$ (X = H, Cl) has been reported to give the corresponding β-aminoacyl complexes as the final

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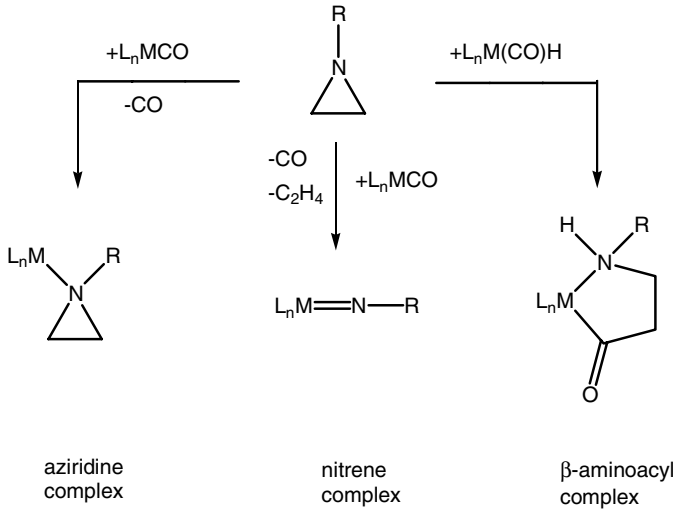
products [7,10] via N-protonation and addition of the opened ring onto the M–C bond of a carbonyl ligand (see Scheme 1). The structures of two further β-aminoacyl complexes have also been reported [11,12].

Electrophilic ring opening reactions of aziridines are well-known in organic chemistry [13] and therefore, aziridines should be reacted with more electrophilic organometallic complex fragments than have previously been used. We chose the easily obtainable chloro complex Ph_3PAuCl (**1**) which is very electrophilic in the presence of AgO_3SCF_3, for reaction with several aziridines. No alkene elimination and no nitrene formation, however, was observed, but again simple *N*-coordination of the aziridines to give the cationic gold(I) complexes $[Ph_3PAuAz]OTf$ (**2**–**8**) (Az = aziridine, 2-methylaziridine, 2,2-dimethylaziridine, 2-ethylaziridine, 2-phenylaziridine, N-benzylaziridine, *N*-hydroxyethylaziridine) was observed.

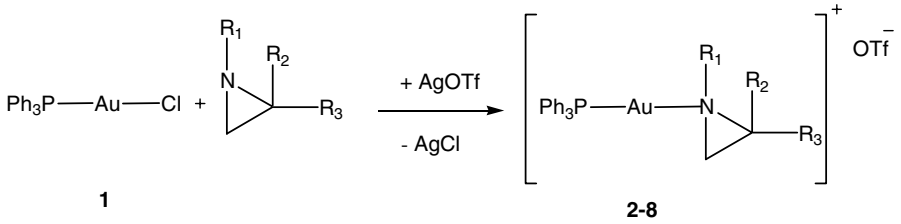
2. Results and discussion

2.1. Synthesis and spectra

The gold(I) complex Ph_3PAuCl (**1**) reacts with stoichiometric amounts (1:1) of the aziridines (Az = C_2H_4NH, C_2H_3MeNH, $C_2H_2Me_2NH$, C_2H_3EtNH, C_2H_3PhNH, C_2H_4NBz, $C_2H_4NC_2H_4OH$) after treatment with CF_3SO_3Ag (=AgOTf) and separation of the precipitated AgCl, to give the ionic monoaziridine complexes $[Ph_3PAuAz]OTf$ (**2**–**8**) in good yields (60–90%, Scheme 2). Without the addition of AgOTf no reaction is observed. Even the strongly electrophilic intermediate $\{Ph_3PAuO_3SCF_3\}$ is unable to induce the desired twofold N–C opening reaction to give either the ionic gold(I) complexes $[Ph_3PAuNX]OTf$ (X = H, R; nitrene stabilisation) or $[Ph_3PAu(C_2H_2X_2)]OTf$ (X = H, R; alkene coordination), respectively. Not even the simple N–C cleavage



Scheme 1. Reaction modes of aziridines with transition metal complexes.



	2	3	4	5	6	7	8
R_1	H	H	H	H	H	Bz	EtOH
R_2	H	Me	Me	Et	Ph	H	H
R_3	H	H	Me	H	H	H	H

Scheme 2. Synthesis of the gold(I)–aziridine complexes **2**–**8**.

reaction of the aziridines, followed by their oxidative addition reaction to give α-iminomethyl complexes is observed. The aziridine complexes **2**–**8** are colourless solids, which melt ($\geqslant 100$ °C) without decomposition, and are air sensitive as well as somewhat light sensitive. They are soluble in polar solvents like acetone or CH_2Cl_2, but insoluble in non-polar ones.

The IR, ^1H, ^{13}C, ^{31}P NMR and mass spectra of compounds **2**–**8** were measured. The IR spectra show almost the same absorptions between 500 and 4000 cm^{-1}, because the compounds all contain both the phenyl groups of the PPh_3 ligand and the aziridine rings in the cations, as well as the same OTf^- anion. Only the spectrum of **8** shows additional absorptions at 3500 cm^{-1} for ν(OH) and 1043 cm^{-1} for ν(C–O). The OTf^- anion is clearly observed by its very strong and characteristic bands at 1150 cm^{-1}–1260 cm^{-1} for ν(CF) and ν(SO).

In the ^1H NMR spectra of the NH-aziridine complexes **2**–**6**, a broad signal is found at 2.83–4.94 ppm for the NH proton. The protons of the CH_2 groups of **2** and **4** appear as singlets at 2.62 ppm, whereas those of **3**, **7** and **8** show two doublets at 2.43 and 2.69 ppm ($^3J = 4.89$ Hz, **3**), 2.92 and 3.14 ppm ($^3J = 4.10$ Hz, **7**), and 2.55 and 3.04 ppm ($^3J = 4.05$ Hz, **8**). Compound **5** shows two double doublets at 2.47 and 2.71 ppm ($^3J \approx 6$ Hz, $^2J = 1.04$ Hz, **5**), whereas **6** shows a broad signal at 3.25 ppm as well as a doublet at 3.07 ppm ($^3J = 7.27$ Hz). The proton in the 2-position of the rings in **3**, **5** and **6** gives either a broad multiplet at 3.04–3.13 ppm (**3**) and 3.07–3.25 ppm (**6**) or a resolved one at 2.99 ppm (ddt, $^3J = 6.90$ and 5.57 Hz, **5**). The *exo*-NCH_2 protons of **7** and **8** are observed as a singlet at 4.27 ppm (**7**) or triplets at 3.13 ppm (t, $^3J = 4.90$ Hz) and 3.99 ppm (t, ^{3}J = 4.75 Hz, CH_2OH, **8**). The proton of the hyrdoxyethyl group in **8** gives a broad signal at 4.71 ppm. The methyl protons in 2-position of **3**–**5** are found at 1.60 ppm (d, $^3J = 5.89$ Hz, **3**), 1.51 and 1.61 ppm (s, **4**) as well as 1.19 ppm (t, $^3J = 7.35$ Hz, **5**). The phenyl protons of the PPh_3 ligands of **2**–**8** and those in the 2-position (**6**), or N-bound (**7**) give multiplets in the same region (7.37–7.76 ppm), whereby assignments were made when possible based on the P–C coupling modes (see Section 4).

In the ^{13}C NMR spectra of **2**, **7** and **8** only one signal is found at 24.6 ppm (**2**), 35.2 (**7**) and 34.5 ppm (**8**) for both ring CH_2 groups, and also one for the CH_2 group in **3** (32.0 ppm), **4** (39.9 ppm), **5** (31.8 ppm), and **6** (30.7 ppm). The C-atom in the 2-position of **3**–**6** gives signals at 34.2 ppm (**3**), 40.9 ppm (**4**), 38.7 ppm (**5**) and 37.6 ppm (**6**). For the N-bound CH_2 groups of **7** and **8**, signals are found at 66.7 ppm (**7**) and 61.1 ppm (**8**), and the O-bound CH_2 group gives a signal at 66.3 ppm (**8**). The phenyl C-atoms in the 2-position of **6** and of the benzyl ligand of **7** show multiplets at 128–137 ppm, and those of the PPh_3 ligands of **2**–**8** in the same region also as multiplets, but with doublet character because of the P–C coupling. The quartet for the CF_3-carbon atom of the OTf^- anion of **2**–**8** is always observed at about 122 ppm (^1J(C,F) ≈ 312 Hz).

In the ^{31}P NMR spectra of **2**–**8** the signals are always found at approximately 31 ppm (e.g. 30.0 ppm (**8**) and 31.3 ppm (**6**)).

In the FAB^+ mass spectra of **2**–**8** the parent signals for the intact cations are measured at $m/z = 502.1$ (**2**), 516.3 (**3**), 530.1 (**4** and **5**), 578.2 (**6**), 592.0 (**7**) and 546.1 (**8**). In all cases, signals for the fragments after cleavage of the aziridine ligands are detected ($[M^+ - Az]$). A peak at $m/z = 721$ for $[Au(PPh_3)_2^+]$, often observed for Ph_3PAu containing species has not been detected. The OTf^- anion present in **2**–**8** gives a signal at $m/z = 149.1$ in the FAB^- mass spectra.

2.2. X-ray structure analyses of 3, 4, 6 and 8

Single Crystals of **3**, **4**, **6** and **8** suitable for X-ray diffraction analyses were obtained by the isothermic diffusion of pentane into CH_2Cl_2 solutions. Relevant data are summarised in Table 1, and the molecular structures together with the most important bond lengths and bond angles are given in Figs. 1–4.

All four compounds have the same linear arrangement at the Au(I) centre with P–Au–N angles between 177.2(11)° (**8**) and 179.5(2)° (**3**), average Au–P distances of about 2.233 Å, and Au–N distances of about 2.08 Å, with the exception of **4** where both distances are somewhat longer (2.278(2) and 2.118(6) Å). This may be due to the steric effect of both Me groups in the 2-position. The N atoms of the aziridines coordinate with their distorted tetrahedral configuration towards the gold(I) centres. Both N–C bond lengths in **4**, **6** and **8** are nearly equal and are about 1.50 Å, whereas those in **3** differ significantly (1.603(13) and 1.381(7) Å), possibly because of the presence of the non-equivalent CH_2 and CHMe moieties. The C–C ring distances of complexes **6** and **8** are very similar (1.478(8) and 1.467(7) Å), whereas those in **3** and **4** differ significantly (1.408(2) and 1.542(2) Å). Again, both the methyl substituted aziridine complexes **3** and **4** show this characteristic. Moreover, although **3** shows the longest N–C and shortest C–C bonds, it was not possible to induce the desired alkene elimination to form the nitrene complex $[Ph_3PAu{=}NH]OTf$. Perhaps the introduction of a bulky substituent on N for kinetic stabilisation reasons is necessary. The planes of the aziridine ligands are bent against the Au–N axis with angles of 66.91° (**3**), 67.98° (**4**), 69.46° (**6**) and 71.24° (**8**).

A look at the molecular structure of **6** (Fig. 3) shows that the phenyl group in the 2-position is very close to the central Au atom, and its ring plane is bent towards the metal. The resulting average distance between Au and the six phenyl C-atoms is about 4.00 Å, which means there is obviously some Au–π-ring interaction due to either electronic reasons or packing effects.

Table 1
Summary of crystallographic data for **3**, **4**, **6** and **8** [14]

Compound	**3**	**4**	**6**	**8**
Empiric formula	$C_{22}H_{22}AuF_3NO_3S$	$C_{23}H_{24}AuF_3NO_3PS$	$C_{27}H_{24}AuF_3NO_3PS$	$C_{23}H_{24}AuF_3NO_4PS$
Formula weight (g mol^{-1})	665.40	679.43	727.47	695.43
Crystal size (mm)	$0.18 \times 0.11 \times 0.04$	$0.20 \times 0.20 \times 0.05$	$0.25 \times 0.10 \times 0.06$	$0.55 \times 0.44 \times 0.40$
Crystal colour, habit	Colourless, plate	Colourless, plate	Colourless, stick	Colourless, prismatic
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	15.003(3)	9.667(7)	8.9911(18)	10.06790(10)
b (Å)	8.9403(18)	9.949(7)	11.599(2)	9.48250(10)
c (Å)	18.710(4)	15.245(11)	26.464(5)	25.9465(2)
α (°)	90	99.807	90	90
β (°)	107.44(3)	106.514(9)	97.16	91.1160 (5)
γ (°)	90	103.370(11)	90	90
V (Å^3)	2394.3(8)	1323.1(16)	1.765	2476.61(4)
Z	4	2	4	4
D_{calc} (g cm^{-3})	1.846	1.705	1.765	1.865
Absorption coefficient (mm^{-1})	6.345	5.743	5.556	6.142
$F(000)$	1288	660	1416	1352
Index ranges	$-17 \leqslant h \leqslant 17$, $-10 \leqslant k \leqslant 10$, $-22 \leqslant l \leqslant 22$	$-11 \leqslant h \leqslant 11$, $-7 \leqslant k \leqslant 7$, $-19 \leqslant l \leqslant 19$	$-11 \leqslant h \leqslant 11$, $-15 \leqslant k \leqslant 14$, $-34 \leqslant l \leqslant 34$	$-11 \leqslant h \leqslant 11$, $-10 \leqslant k \leqslant 10$, $-29 \leqslant l \leqslant 29$
θ Range (°)	3.23–25.08	1.44–27.15	3.13–27.47	1.57–24.00
Reflections collected	26421	6980	46429	24884
Independent reflections	4237	3545	6240	3895
Observed reflections	2932	3084	4939	3168
Parameter/restrains	285/0	304/0	334/0	311/0
R_1/wR_2 (all data)	0.0772/0.1082	0.0480/0.0976	0.0602/0.0963	0.0380/0.1105
R_1/wR_2 (final)	0.0443/0.0962	0.0405/0.0943	0.0407/0.0893	0.0280/0.0960
Goodness-of-fit	1.035	1.050	1.039	1.147
Minimum/maximum ρ_e (e Å^{-3})	−1.764/1.131	−2.515/1.066	−1.645/3.731	−2.325/0.933
T (K)	200(2)	200(2)	200(2)	200(2)
Diffractometer used	Nonius Kappa CCD	Siemens SMART Area-detector	Nonius Kappa CCD	Nonius Kappa CCD
Scan type	Area detection	Area detection	Area detection	Area detection
Solution	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97
Refinement	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97
Deposit number	255032	254788	255033	255030

A very similar effect is observed in compound **8** (Fig. 4) with the N-bound hydroxyethyl group. The O-atom of the hydroxy group lies very close to the Au centre, with the short Au–O distance of 3.078 Å, which is significantly shorter than the sum of the van der Waal radii. The short Au–O distance observed in **8** arises even although there is no deviation from linearity of the P–Au–N moiety and no peculiar Au–Au interaction. Interestingly, despite these observations no significant shifts of the corresponding signals in the IR or ^{1}H and ^{13}C NMR spectra of **6** and **8** were observed.

3. Conclusions

The synthesis of the new complexes **2**–**8** indicates that even the strong electrophilic complex $\{Ph_3PAuO_3SCF_3\}$, which is the resulting intermediate in the reaction of Ph_3PAuCl (**1**) with CF_3SO_3Ag, cannot cleave *one* or *both* N–C bonds of the aziridines. Therefore, with respect to the first case, **1** does not appear to be active as a catalyst for the cationic induced polymerisation reaction of aziridines ($(-N(R)-CH_2-CH_2-)_n$). Compound **1** is also unsuitable to undergo an oxidative addition reaction leading to α-iminomethyl complexes of gold(III) ($H-Au^+-CH_2-CH{=}NR$). With respect to the cleavage of both N–C bonds, **1** cannot be used for the synthesis of nitrene complexes ($Au{=}N-R$). This is surprising because the use of gold(I) complexes in catalysis is steadily increasing. Because in special cases [7,10–12] one N–C bond has been opened to give β-aminoacyl complexes, further investigations should be focussed on influencing the reactivity of aziridine ligands by using suitable substituents at N- or C-atoms.

4. Experimental

4.1. General procedures

All operations were carried out under Ar in dry solvents. Ph_3PAuCl (**1**) was prepared according to the

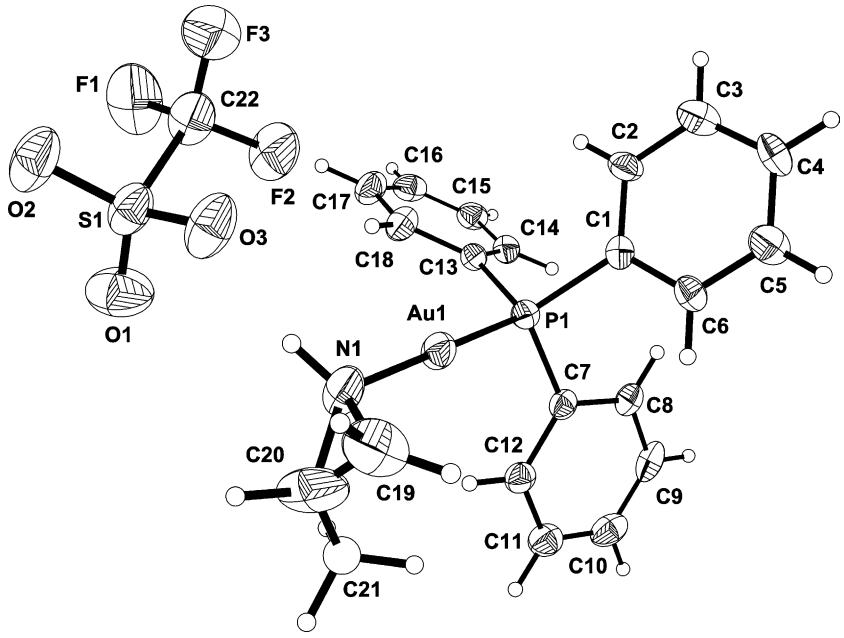


Fig. 1. Molecular structure of **3**: selected bond lengths (Å) and angles (°): Au(1)–N(1) 2.073(6), Au–P(1) 2.231(2), N(1)–C(19) 1.603(13), N(1)–C(20) 1.381(7), C(19)–C(20) 1.408(19), C(20)–C(21) 1.307(17); N(1)–Au(1)–P(1) 179.5(2), C(19)–N(1)–C(20) 55.7(8), C(19)–N(1)–Au(1) 125.1(6), C(20)–N(1)–Au(1) 128.1(7), N(1)–C(20)–C(19) 54.1(6), N(1)–C(20)–C(21) 113.6(11).

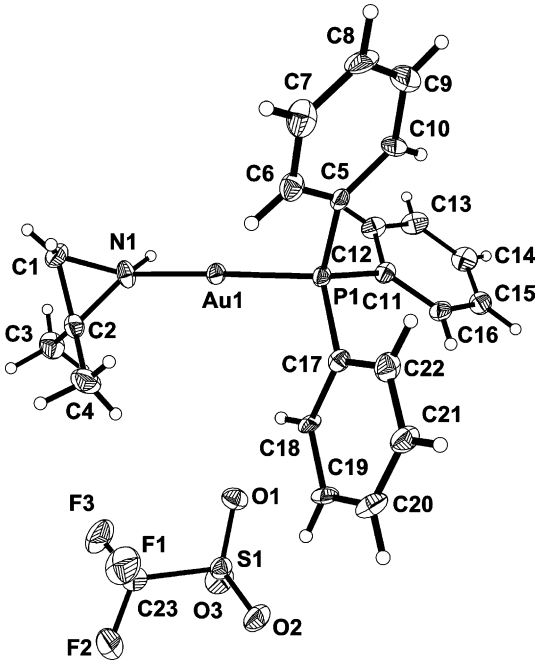


Fig. 2. Molecular structure of **4**: selected bond lengths (Å) and angles (°): Au(1)–N(1) 2.118(6), Au(1)–P(1) 2.278(2), N(1)–C(2) 1.513(10), N(1)–C(1) 1.540(12), C(1)–C(2) 1.542(14), C(2)–C(4) 1.517(12), C(2)–C(3) 1.531(12); N(1)–Au(1)–P(1) 178.4(2), C(2)–N(1)–C(1) 60.7(6), C(2)–N(1)–Au(1) 122.6(5), C(1)–N(1)–Au(1) 122.7(5), N(1)–C(1)–C(2) 58.8(6), N(1)–C(2)–C(4) 115.3(6), N(1)–C(2)–C(3) 114.0(7), C(4)–C(2)–C(3) 117.9(10), N(1)–C(2)–C(1) 60.5(6), C(4)–C(2)–C(1) 117.7(8), C(3)–C(2)–C(1) 118.3(8).

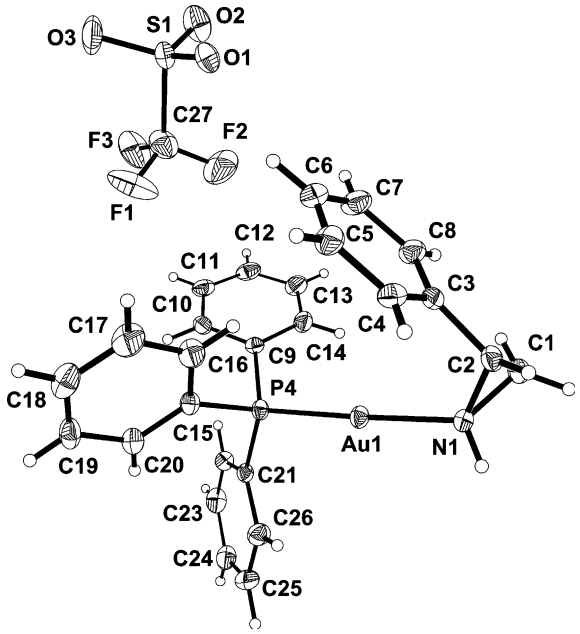


Fig. 3. Molecular structure of **6**: selected bond lengths (Å) and angles (°): Au(1)–N(1) 2.082(4), Au(1)–P(4) 2.2368(15), N(1)–C(2) 1.504(7), N(1)–C(1) 1.467(7), C(1)–C(2) 1.478(8), C(2)–C(3) 1.494(8), C(3)–C(4) 1.387(8); N(1)–Au(1)–P(4) 178.04(13), C(1)–N(1)–C(2) 59.4(4), C(2)–N(1)–Au(1) 119.3(3), C(1)–N(1)–Au(1) 124.0(4), N(1)–C(1)–C(2) 61.5(4), N(1)–C(2)–C(3) 116.1(4), C(1)–C(2)–N(1) 61.5(4).

literature procedure [15,16]. *N*-Hydroxyethylaziridine was purchased from Acros. 2-Methylaziridine, 2,2-dimethylaziridine, 2-ethylaziridine, 2-phenylaziridine and *N*-benzylaziridine were prepared according to the literature procedure [17–21]. NMR spectra were recorded on a Jeol 270 spectrometer (^{1}H: 270.17 MHz, ^{13}C: 67.94 MHz and ^{31}P: 109.37 MHz) in [D_6]-acetone. Mass spectra were obtained on a Jeol Mstation JMS 700. IR

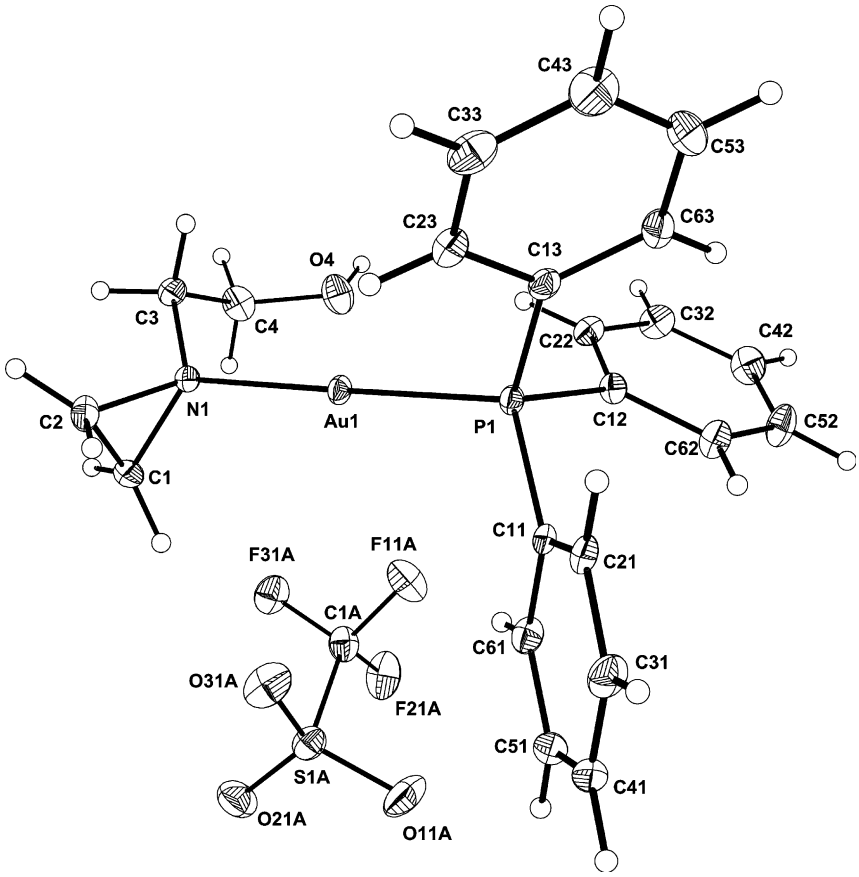


Fig. 4. Molecular structure of **8**: selected bond lengths (Å) and angles (°): Au–N 2.090(6), Au(1)–P(1) 2.2327(17), N(1)–C(3) 1.475(6), N(1)–C(1) 1.485(7), N(1)–C(2) 1.494(7), C(1)–C(2) 1.467(7), C(3)–C(4) 1.489(7), C(4)–O(4) 1.420(6); N(1)–Au(1)–P(1) 177.25(14), C(3)–N(1)–C(1) 113.8(5), C(3)–N(1)–C(2) 114.4(5), C(1)–N(1)–C(2) 59.0(3), C(3)–N(1)–Au(1) 117.3(3), C(1)–N(1)–Au(1) 121.5(3), C(2)–N(1)–Au(1) 117.8(3), C(2)–C(1)–N(1) 60.8(4), C(1)–C(2)–N(1) 60.2(3), N(1)–C(3)–C(4) 112.8(5), O(4)–C(4)–C(3) 111.6(4).

spectra were measured on a Perkin–Elmer Spectrum One FT-IR-spectrometer. Elemental analyses were performed on a Heraeus Elementar Vario EL.

4.1.1. General procedure

Ph_3PAuCl (**1**) was dissolved in 20 ml of dichloromethane, AgOTf was added and the solution was stirred for 15 min until all the AgCl had precipitated. After centrifugation and separation of the solution by decantation, a small excess of the aziridine was added. After stirring the solution for about 1 h, the solvent was evaporated, and the colourless residue was purified by stirring in n-hexane, followed by filtration and drying the colourless solid in vacuo.

4.2. [Aziridine-triphenylphosphanegold(I)]-trifluormethylsulfonate (**2**)

113.0 mg (0.235 mmol) Ph_3PAuCl (**1**), 66.0 mg (0.258 mmol) AgOTf, 10.0 μl (0.258 mmol) aziridine. Yield: 99.5 mg (0.153 mmol, 65%), colourless powder; m.p. 115–117 °C. ^{1}H NMR ([D$_6$]-acetone, 270.17 MHz): δ 2.62 (s, 4 H, Az–CH_2), 2.83 (br, 1 H, NH), 7.61–7.65 (m, 15 H, $CH_{arom.}$). ^{13}C NMR ([D$_6$]-acetone, 67.94 MHz): δ 24.6 (Az–CH_2), 122.1 (q, ^1J(C,F) = 321.65 Hz, CF_3), 128.2 (d, ^1J(C,P) = 64.37 Hz, $CH_{arom.}$), 130.0 (d, ^3J(C,P) = 12.66 Hz, *m*-$CH_{arom.}$), 132.9 (d, ^4J(C,P) = 3.12 Hz, *p*-$CH_{arom.}$), 134.6 (d, ^2J(C,P) = 14.54 Hz, *o*-$CH_{arom.}$). ^{31}P NMR ([D$_6$]-acetone, 109.37 MHz): δ 30.8 (PPh_3). IR (KBr) [cm^{-1}]: 3260 (w), 3085 (w), 3048 (w), 2960 (w), 2923 (w), 2857 (w), 1622 (w), 1591 (w), 1576 (w), 1482 (m), 1437 (s), 1333 (w), 1259 (vs), 1228 (m), 1161 (s), 1103 (s), 1120 (w), 1103 (s), 1073 (w), 1031 (vs), 998 (w), 931 (w), 856 (w), 750 (m), 712 (m), 694 (s), 654 (m), 638 (s), 574 (w), 544 (s), 510 (m), 452 (w). Elemental analysis (%) $C_{21}H_{20}AuF_3NO_3PS$ (651.39): calc. C, 38.73; H, 3.09; N, 2.15; found: C, 39.23; H, 3.43; N, 2.50%. MS (FAB$^+$): *m/z* (%) = 502.1 (79) [M$^+$], 459.1 (100) [M$^+$ − Az].

4.3. [2-Methylaziridine-triphenylphosphanegold(I)]-trifluomethylsulfonate (**3**)

85.0 mg (0.172 mmol) Ph_3PAuCl (**1**), 49.0 mg (0.189 mmol) AgOTf, 61.3 μl (0.189 mmol) 2-methylaziridine. Yield: 97.0 mg (0.146 mmol, 85%), colourless crystals;

m.p. 110 °C. ^{1}H NMR ([D$_6$]-acetone, 270.17 MHz): δ 1.60 (d, ^3J = 5.81 Hz, 3 H, CH$_3$), 2.43 (d, ^{3}J = 4.89, 1 H, Az–CH$_2$), 2.69 (d, ^3J = 4.89 Hz, 1 H, Az–CH$_2$), 3.04–3.13 (m, 1 H, Az–CH), 7.57–7.76 (m, 15 H, CH$_{arom.}$). ^{13}C NMR ([D$_6$]-acetone, 67.94 MHz) δ 19.4 (CH$_3$), 32.0 (Az–CH$_2$), 34.2 (Az–CH$_2$), 122.3 (q, ^1J(C,F) = 321.64 Hz, CF$_3$), 127.9 (d, ^1J(C,P) = 64.37 Hz, CH$_{arom.}$), 129.8 (d, ^3J(C, P) = 12.46 Hz, *m*-CH$_{arom.}$), 132.9 (d, ^4J(C,P) = 3.11 Hz, *p*-CH$_{arom.}$), 134.3 (d, ^2J(C,P) = 13.50 Hz, *o*-CH$_{arom.}$). ^{31}P NMR ([D$_6$]-acetone, 109.37 MHz) δ 31.2 (PPh$_3$). IR (KBr) [cm^{-1}]: 3172 (m), 3056 (w), 3016 (w), 2990 (w), 2928 (w), 2864 (w), 1627 (m), 1586 (w), 1574 (w), 1480 (m), 1437 (vs), 1408 (w), 1372 (w), 1330 (w), 1275 (vs), 1256 (vs), 1226 (s), 1165 (vs), 1102 (s), 1046 (s), 1028 (vs), 998 (m), 927 (w), 845 (w), 748 (s), 713 (s), 693 (vs), 656 (s), 637 (s), 545 (s), 501 (s). Elemental analysis (%) C$_{22}$H$_{22}$AuF$_3$NO$_3$PS (679.45): calc. C, 39.71; H, 3.33; N, 2.10; S, 4.82; found: C, 40.35; H, 3.35; N, 2.21; S, 4.81%. MS (FAB$^+$): *m*/*z* (%) = 516.3 [M$^+$] (100), 459.2 [M$^+$ − Az] (95).

4.4. [2,2-Dimethylaziridine-triphenylphosphanegold(I)]-trifluormethylsulfonate (4)

167.0 mg (0.336 mmol) Ph$_3$PAuCl (**1**), 98.3 mg (0.381 mmol) AgOTf, 30.7 μl (0.258 mmol) 2,2-dimethylaziridine. Yield: 211.0 mg (0.311 mmol, 92%), colourless crystals; m.p. 129 °C. ^{1}H NMR ([D$_6$]-acetone, 270.17 MHz): δ 1.54 (s, 3 H, CH$_3$), 1.61 (s, 3 H, CH$_3$), 2.61 (s, 2 H, Az–CH$_2$), 4.43 (br, 1 H, NH), 7.59–7.69 (m, 15 H, CH$_{arom.}$). ^{13}C NMR ([D$_6$]-acetone, 67.94 MHz): δ 23.5 (CH$_3$), 26.3 (CH$_3$), 39.9 (Az–CH$_2$), 40.9 (C$_q$), 122.2 (q, ^1J(C,F) = 321.63 Hz, CF$_3$), 128.7 (d, ^1J(C,P) = 63.84 Hz, C$_q$), 130.5 (d, ^3J(C,P) = 12.0 Hz, *m*-CH$_{arom.}$), 133.4 (d, ^4J(C,P) = 2.24 Hz, *p*-CH$_{arom.}$), 135.0 (d, ^2J(C,P) = 13.72 Hz, *o*-CH$_{arom.}$). ^{31}P NMR ([D$_6$]-acetone, 109.37 MHz): δ 31.2 (PPh$_3$). IR (KBr) [cm^{-1}]: 3172 (w), 3055 (w), 2975 (w), 2923 (w), 2850 (w), 1629 (m), 1588 (s), 1482 (w), 1437 (vs), 1390 (m), 1333 (m), 1282 (vs), 1252 (vs), 1226 (s), 1167 (vs), 1103 (s), 1047 (vs), 1028 (vs), 998 (m), 912 (w), 806 (w), 751 (s), 713 (s), 694 (vs), 656 (vs), 638 (vs), 544 (vs), 510 (s). Elemental analysis (%) C$_{23}$H$_{24}$AuF$_3$NO$_3$PS (679.45): calc. C, 40.66; H, 3.56; N, 2.06; found: C, 40.02; H, 3.42; N, 2.07%. MS (FAB$^+$): *m*/*z* (%) = 530.1 (100) [M$^+$], 459.1 (28) [M$^+$ − Az].

4.5. [2-Ethylaziridine-triphenylphosphanegold(I)]-trifluormethylsulfonate (5)

88.9 mg (0.185 mmol) Ph$_3$PAuCl (**1**), 49.2 mg (0.192 mmol) AgOTf, 16.6 μl (0.190 mmol) 2-ethylaziridine. Yield: 105.0 mg (0.155 mmol, 82%), colourless powder; m.p. 97 °C. ^{1}H NMR ([D$_6$]-acetone, 270.17 MHz): δ 1.19 (t, ^3J = 7.35 Hz, 3 H, CH$_3$), 1.82 (dq, ^3J = ^3J = 7.27 Hz, 2 H, CH$_2$), 2.47 (dd, ^3J = 5.27 Hz, ^2J = 1.04 Hz, 1 H, Az–CH$_2$), 2.71 (dd, ^3J = 6.75 Hz, ^2J = 1.04 Hz, 1 H, Az–CH$_2$), 2.99 (ddt, ^3J = 6.90 Hz, ^3J = 5.57 Hz, 1 H, Az–CH), 4.62 (br, 1 H, NH), 7.58–7.72 (m, 15 H, CH$_{arom.}$). ^{13}C NMR ([D$_6$]-acetone, 67.94 MHz): δ 11.4 (CH$_3$), 28.1 (CH$_2$), 31.8 (Az–CH$_2$), 38.7 (Az–CH), 122.2 (q, ^1J(C,F) = 321.53 Hz, CF$_3$), 128.6 (d, ^1J(C,P) = 64.10 Hz, CH$_{arom.}$), 130.5 (d, ^3J(C,P) = 11.94 Hz, *m*-CH$_{arom.}$), 133.4 (d, ^4J(C,P) = 2.60 Hz, *p*-CH$_{arom.}$), 135.0 (d, ^2J(C,P) = 13.49 Hz, *o*-CH$_{arom.}$). ^{31}P NMR ([D$_6$]-acetone, 109.37 MHz): δ 31.2 (PPh$_3$). IR (KBr) [cm^{-1}]: 3180 (m), 3055 (w), 311 (w), 2960 (w), 2931 (w), 2872 (w), 1618 (w), 1588 (w), 1574 (w), 1480 (w), 1438 (w), 1380 (w), 1336 (w), 1288 (vs), 1252 (vs), 1226 (s), 1164 (s), 1102 (vs), 1048 (s), 1029 (vs), 998 (m), 923 (w), 843 (w), 749 (vs), 713 (s), 694 (vs), 657 (s), 637 (vs), 574 (m), 545 (vs), 500 (s). Elemental analysis (%) C$_{23}$H$_{24}$AuF$_3$NO$_3$PS (679.45): calc. C, 40.66; H, 3.56; N, 2.06; found: C, 40.85; H, 3.72; N, 2.06%. MS (FAB$^+$): *m*/*z* (%) = 530.1 (100) [M$^+$], 459.1 (33) [M$^+$ − Az].

4.6. [2-Phenylaziridine-triphenylphosphanegold(I)]-trifluormethylsulfonate (6)

136.2 mg (0.283 mmol) Ph$_3$PAuCl (**1**), 80.0 mg (0.311 mmol) AgOTf, 36.0 μl (0.311 mmol) 2-phenylaziridine. Yield: 125.3 mg (0.173 mmol, 61%), colourless powder; m.p. 120–123 °C. ^{1}H NMR ([D$_6$]-acetone, 270.17 MHz): δ 3.07 (d, ^3J = 7.27 Hz, 1 H, Az–CH$_2$), 3.25 (br, 1 H, Az–CH$_2$), 4.10 (t, ^3J = 6.38 Hz, 1 H, Az–CH), 4.94 (br, 1 H, NH), 7.37–7.45 (m, 5 H, CH$_{arom.}$), 7.46–7.65 (m, 15 H, CH$_{arom.}$). ^{13}C NMR ([D$_6$]-acetone, 67.94 MHz) δ 30.7 (Az–CH$_2$), 37.6 (Az–CH$_2$), 128.1 (d, ^1J(C,P) = 65.39 Hz, CH$_{arom.}$), 128.5 (CH$_{arom.}$), 128.7 (CH$_{arom.}$), 129.4 (CH$_{arom.}$), 129.5 (CH$_{arom.}$), 129.9 (d, ^3J(C,P) = 12.46 Hz, *m*-CH$_{arom.}$), 132.3 (CH$_{arom.}$), 132.8 (d, ^4J(C,P) = 3.11 Hz, *p*-CH$_{arom.}$), 134.4 (d, ^2J(C,P) = 13.49 Hz, *o*-CH$_{arom.}$). ^{31}P NMR ([D$_6$]-acetone, 109.37 MHz) δ 31.3 (PPh$_3$). IR (KBr) [cm^{-1}]: 3261 (w), 3057 (w), 1635 (m), 1606 (m), 1496 (w), 1481 (w), 1437 (s), 1396 (w), 1333 (w), 1257 (vs), 1167 (s), 1102 (m), 1071 (w), 1031 (s), 998 (w), 889 (w), 862 (w), 754 (m), 712 (m), 694 (s), 638 (s), 575 (w), 544 (s), 509 (m). Elemental analysis (%) C$_{27}$H$_{24}$AuF$_3$NO$_3$PS (727.47): calc. C, 44.58; H, 3.30; N, 1.93; found: C, 45.51; H, 3.41; N, 2.24%. MS (FAB$^+$): *m*/*z* (%) = 578.2 (100) [M$^+$], 469.2 (60) [M$^+$ − Az].

4.7. [N-Benzylaziridine-triphenylphosphanegold(I)]-trifluormethylsulfonate (7)

105.3 mg (0.219 mmol) Ph$_3$PAuCl (**1**), 56.7 (0.221 mmol) AgOTf, 30.2 μl (0.220 mmol) *N*-benzylaziridine. Yield: 142.0 mg (0.191 mmol, 86%), colourless powder; m.p. 96 °C. ^{1}H NMR ([D$_6$]-acetone, 270.17 MHz): δ 2.92 (d, *J* = 4.08 Hz, 2 H, Az–CH$_2$), 3.14 (d, *J* = 4.15

Hz, 2 H, Az–CH_2), 4.22 (s, 2 H, Ph-CH_2), 7.36–7.45 (m, 5 H, Bz–H), 7.54–7.75 (m, 15 H, $CH_{arom.}$). ^{13}C NMR ([D_6]-acetone, 67.94 MHz): δ 35.2 (Az–CH_2), 66.7 (Ph-CH_2-N), 122.4 (q, ^1J(C,F) = 322.34 Hz, CF_3), 128.4 (d, ^1J(C,P) = 66.05 Hz, $C_{q,\ arom.}$), 129.9 (*p*-Bz–C), 129.9 (*o*-Bz–C), 130.4 (d, ^3J(C,P) = 11.94 Hz, *m*-$CH_{arom.}$), 130.6 (*m*-Bz–C), 133.3 (d, ^4J(C,P) = 2.34 Hz, *p*-$CH_{arom.}$), 134.9 (d, ^2J(C,P) = 13.49 Hz, *o*-$CH_{arom.}$), 137.7 (Bz–C_q). ^{31}P NMR ([D_6]-acetone, 109.37 MHz) δ 30.2 (PPh_3). IR (KBr) [cm^{-1}]: 3063 (w), 3026 (w), 2989 (w), 2923 (w), 2814 (w), 1605 (w), 1586 (w), 1495 (m), 1481 (m), 1438 (s), 1331 (w), 1260 (vs), 1224 (s), 1155 (s), 1102 (vs), 1047 (s), 1031 (vs), 998 (m), 923 (w), 869 (w), 823 (w), 748 (vs), 713 (s), 693 (vs), 656 (s), 637 (vs), 572 (m), 545 (vs), 501 (s). Elemental analysis (%) $C_{28}H_{26}AuF_3NO_3PS$ (741.52): calc. C, 45.35; H, 3.53; N, 1.89; found: C, 46.59; H, 3.78; N, 2.14%. MS (FAB^+): *m*/*z* (%) = 592.0 (28) [M^+], 459 (21) [M^+ − Az].

4.8. [*N*-Hydroxyethylaziridine-triphenylphosphane-gold(I)]trifluormethylsulfonate (**8**)

87.1 mg (0.235 mmol) Ph_3PAuCl (**1**), 66.5 mg (0.259 mmol) AgOTf, 20.1 μl (0.259mmol) *N*-hydroxyethylaziridine. Yield: 112.0 mg (0.161 mmol, 88%), colourless crystals; m.p. 118 °C. ^1H NMR ([D_6]-acetone, 270.17 MHz): δ 2.55 (d, ^3J = 4.01 Hz, 2 H, Az–CH_2), 3.04 (d, ^3J = 4.08 Hz, 2 H, Az–CH_2), 3.13 (t, ^3J = 4.90 Hz, 3 H, N–CH_2), 3.99 (t, ^3J = 4.75 Hz, 3 H, CH_2OH), 4.71 (br, 1 H, OH), 7.50–7.72 (m, 15 H, $CH_{arom.}$). ^{13}C NMR ([D_6]-acetone, 67.94 MHz): δ 34.5 (Az–CH_2), 61.1 (N–CH_2), 66.3 (CH_2OH), 122.3 (q, ^1J(C,F) = 321.09 Hz, CF_3), 128.8 (d, ^1J(C,P) = 67.99 Hz, $C_{q,\ arom.}$), 130.4 (d, ^3J(C,P) = 11.94 Hz, *m*-$CH_{arom.}$), 133.3 (d, ^4J(C,P) = 2.34 Hz, *p*-$CH_{arom.}$), 135.1 (d, ^2J(C,P) = 13.75 Hz, *o*-$CH_{arom.}$). ^{31}P NMR ([D_6]-acetone, 109.37 MHz): δ 30.0 (PPh_3). IR (KBr) [cm^{-1}]: 3502 (s), 3072 (w), 3050 (w), 2989 (w), 2953 (w), 2828 (w), 1630 (w), 1588 (w), 1574 (w), 1480 (s), 1436 (s), 1364 (w), 1330 (w), 1261 (vs), 1231 (s), 1176 (s), 1103 (vs), 1043 (vs), 999 (m), 936 (w), 882 (w), 748 (vs), 713 (s), 693 (vs), 652 (s), 579 (w), 545 (vs), 501 (s), 449 (w). Elemental analysis (%) $C_{23}H_{24}AuF_3NO_4PS$ (695.45): calc. C, 39.72; H, 3.48; N, 2.01; found: C, 40.33; H, 3.50; N, 2.05%. MS (FAB^+): *m*/*z* (%) = 546.1 (35) [M^+], 459 (88) [M^+ − Az].

4.9. Thermal and photolytic experiments for alkene elimination of **2**–**8**

All compounds were dissolved in CH_2Cl_2 and kept under reflux conditions for about 1 h. The clear solutions were then worked up as described above, and the original complexes **2**–**8** were obtained.

Solutions of **2**–**8** in THF were irradiated with a UV lamp (Hg, 125 W) for about 2 h. The same work-up of the solutions yielded the original compounds **2**–**8**. In both cases, no alkene elimination and no formation of the desired nitrene complexes was observed.

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[14] Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 255032 for compound **3**, CCDC No. 254788 for compound **4**, CCDC No. 255033 for compound **6**, CCDC No. 255030 for compound **8**. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 033 or e-mail deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk].

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