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Synthesis and Characterization of Thienyl Oligomeric, Carbene, and Nitrogen-Donor Complexes of Gold(I)[†]

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Reaction of [AuCl(tht)] (tht = tetrahydrothiophene) with 2-(4′,5′-dihydro-4′,4′-dimethyl-2′-oxazolinyl)thien-5-yllithium or 2-(4′,5′-dihydro-4′,4′-dimethyl-2′-oxazolinyl)thien-3-yllithium afforded thienyl dimeric and trimeric oligomers of gold(I). Protonation of these compounds as well as the stable monomers obtained from [Au(C_6F_5)(tht)] or [AuCl(PPh_3)] afforded unique diorganocarbene complexes as well as nitrogen-donor compounds, the former being unusual divinylcarbene complexes. Reaction of 2-(2′-pyridyl)thien-5-yllithium with [AuCl(PPh_3)] produced, upon alkylation, organothiocarbene compounds. The molecular structure of the dimeric compound $[Au\{C{=}C(C{=}NCMe_2CH_2O)SCH{=}CH\}]_2$ shows a Au···Au separation of 2.8450(6) Å.

Introduction

Carbene complexes of gold are accessible by mainly four types of transformation, namely the addition of alcohols or amines to coordinated isocyanides,[1,2] the cleavage of electron-rich olefins,[3] carbene transfer from tungsten, molybdenum, or chromium pentacarbonyl complexes,[4] and protonation or alkylation of gold azolyl compounds.[5−9]

The latter method, developed in our laboratory, involves the addition of gold(I) chloride or (tetrahydrothiophene)(pentafluorophenyl)gold complexes to lithiated azoles, such as thiazoles,[5,6] imidazoles,[9] pyrazoles, and isothiazole,[7] as well as lithiated pyridine.[8] These precursor complexes are then alkylated or protonated to form aminothio-, diamino-, organothio- as well as aminoorganocarbene complexes. In the thiazolinylidene, imidazolinylidene, and pyridinylidene complexes, the nucleophilic nitrogen atom is situated α to the coordinated carbon atom, while in the isothiazolinylidene and pyrazolinylidene complexes, this nitrogen atom is situated in the γ position. In all of the above methods of synthesis, however, the isolated carbene complexes contain at least one α heteroatom.

Utilizing the consecutive transmetalation−alkylation or −protonation approach, but using different bicyclic organic compounds, we have now been able to synthesize carbene complexes in which the nucleophilic heteroatom in the precursor complex is located outside the coordinated ring system and is separated from the coordinated carbon by several bonds. More importantly, this procedure has also led to the synthesis of the first gold carbene complexes that contain no α heteroatom and also to the synthesis of oligomeric 6-membered and 18-membered thienyl gold compounds.

Lithiation of the bifunctional 4′,5′-dihydro-4′,4′-dimethyl-2′-(2-thienyl)oxazoline[10] compound at C^3 or C^5 unexpectedly led to the isolation of fascinating dimeric and trimeric gold complexes. The crystal and molecular structure of both complexes were determined by X-ray single-crystal diffraction methods. However, only the structure of the former complex will be discussed here. Most known bicyclic Au(I) compounds are derived from phosphorus ylides and have been widely studied, mainly in the research groups of Schmidbaur[11] and Fackler,[12] due to the Au···Au attractive interactions which they display. The new dimeric thienyl gold complex also has a short Au···Au separation of 2.845(6) Å.

Protonation of the dimeric gold compound led to the formation of a *bis*(carbene) complex, albeit in low yield, as well as a nitrogen coordinated complex. Since the products between [AuCl(PPh_3)] or [Au(C_6F_5)(tht)] (tht = tetrahydrothiophene) and lithiated 2-(2′-oxazolinyl)-thien-3-yllithium should not necessarily oligomerize, this alternative route was investigated toward the preparation of carbene complexes, both of which are without any α heteroatom. In contrast, lithiation in the C^5 position produced an imine complex. Finally, reaction with 2-(2′-pyridyl)thien-5-yllithium afforded, after alkylation, an organothiocarbene complex of gold.

It is not an easy task to choose the correct terminology as well as the correct manner in which the new ‘carbene complexes’ should be represented. Definitions such as

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[†] Dedicated to Prof. Dieter Seebach on the occasion of his 60th birthday.

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'a carbene molecule attached to a substrate'[13] and 'ligands bound through a disubstituted carbon atom'[14] have been used. This terminology has been used even though these complexes neither give rise to nor are made from free carbenes. Most authors draw a metal−carbon double bond,[15] others use Lewis adducts (with arrows),[7,16] and some draw a dipolar metal−carbon double bond (Lewis structure)[17] to represent these so-called carbene complexes. Still, other authors draw single bonds between all of the atoms bonded to the carbene carbon.[18] There is general consensus that π-back-donation in carbene, carbonyl, and isocyanide complexes of gold occurs only to a limited extent,[19,20] and thus, representation of these compounds by a metal−carbon double bond is certainly inaccurate. In this paper, we have chosen to call a number of the new compounds carbene complexes and have chosen to represent them by single metal−carbon bonds, as well as positive charges being located on the nitrogen atoms. Heterolytic metal−carbon bond cleavage would afford ligands which can be written in the form of free carbenes.

Results and Discussion

The spectroscopic data for all of the new compounds described are collected in Tables 1 and 2 and are discussed where relevant. To simplify the drawings in the schemes, the counter ion, $CF_3SO_3^-$, is not included when cationic complexes are displayed. In assigning the spectroscopic data below, the numbering in Scheme 1 and Scheme 5 was used.

(Thienyl)oxazoline Binuclear, Trinuclear, Nitrogen-Donor, and Carbene Complexes of Gold. The reaction of 2-(4′,5′-dihydro-4′,4′-dimethyloxazolin-2′-yl)thien-3-yllithium with 1 equiv of [AuCl(tht)] at −60 °C in diethyl ether afforded, after crystallization, the neutral dimeric gold compound **1** (Scheme 1). The yellow crystals were suitable for an X-ray crystallographic investigation. Attempts to form the bis(thienyl)aurate compound **1a** by adding two or more equivalents of the lithiated bicyclic compound also only resulted in the formation of the dimer **1** (Scheme 1).

Protonation of the cyclic compound **1** at −60 °C with 2 molar equiv of CF_3SO_3H afforded the nitrogen-coordinated (thienyl)oxazoline complex **2** (Scheme 1). The solvent was removed, and complex **2** was extracted with methylene chloride, filtered through Celite, and crystallized at −20 °C. A ^{1}H NMR study of the reaction mixture before crystallization showed the presence of the unreacted dimer **1**, the diimine complex **2**, and the cationic carbene complex **3** (Scheme 1). The carbene

Table 1. ^{1}H NMR Data[a]

	H^3	H^4	H^5	CH_2	CMe_2	other
1		7.26 (2H, d, *J* = 4.80)	7.54 (2H, d, *J* = 4.82)	4.32 (4H, s)	1.58 (12H, s)	
2	8.38 (2H, m)	7.48 (2H, dd, *J* = 3.90, *J* = 4.80)	8.38 (2H, m)	5.05 (4H, s)	1.74 (12H, s)	
3		7.32 (2H, d, *J* = 4.80)	8.09 (2H, d, *J* = 4.80)	4.94 (4H, s)	1.74 (12H, s)	10.99 (2H, br s, NH)
4	7.92 (3H, d, *J* = 3.66)	7.05 (3H, d, *J* = 3.66)		4.35 (6H, s)	1.61 (18H, s)	
5	8.44 (1H, dd, *J* = 4.20, *J* = 1.22)	7.32 (1H, dd, *J* = 5.10, *J* = 4.20)	8.01 (1H, dd, *J* = 4.80, *J* = 0.90)	4.74 (2H, s)	1.68 (6H, s)	12.62 (1H, br s, NH)
6		7.22 (1H, d, *J* = 4.74)	7.52 (10H, m)	4.07 (2H, s)	1.33 (6H, s)	7.67 (6H, m, H_{ortho}) 7.52 (10H, m, H_{meta}, H_{para})
7		7.44 (1H, d, *J* = 6.60)	8.27 (1H, d, *J* = 4.68)	4.65 (2H, s)	1.63 (6H, s)	7.76 (15H, m, Ph)
8		7.44 (1H, d, *J* = 4.80)	8.09 (1H, d, *J* = 4.50)	4.84 (2H, s)	1.67 (6H, s)	10.89 (1H, br s)
9	8.20 (1H, dd, *J* = 3.90, *J* = 1.50)	7.28 (1H, dd, *J* = 5.10, *J* = 3.90)	8.02 (1H, dd, *J* = 4.80, *J* = 1.20)	4.63 (2H, s)	1.64 (6H, s)	

	H^3	H^4	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$	other
10	7.87 (1H, d, *J* = 3.48)	7.14 (1H, d, *J* = 3.46)	7.61 (17H, m)	7.61 (17H, m)	7.06 (1H, ddd, *J* = 3.36, *J* = 4.88, *J* = 9.76)	8.52 (1H, dt, *J* = 1.18, *J* = 4.84)	7.61 (17H, m, Ph)
11	7.93 (1H, d, *J* = 3.64)	7.32 (1H, d, *J* = 3.72)	8.02 (1H, dd, *J* = 1.22, *J* = 6.88)	8.33 (1H, td, *J* = 1.22, *J* = 7.58)	7.76 (1H, td, *J* = 1.40, *J* = 6.16)	8.86 (1H, d, *J* = 6.10)	7.55 (15H, m) 4.43 (3H, s)

[a] Chemical shifts are given in parts per million and coupling constants (*J*) in hertz.

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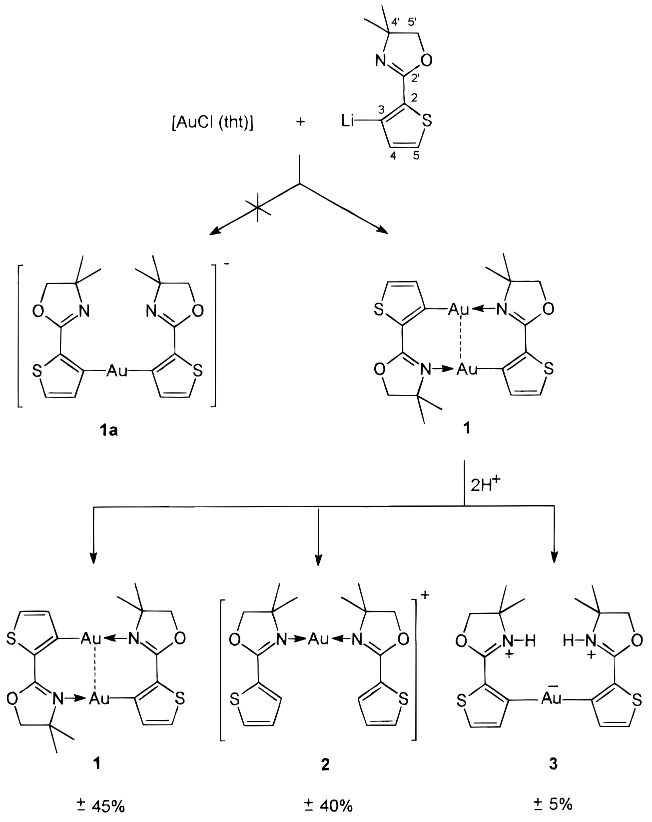
Table 2. ^{13}C NMR Data[a]

	C^2	C^3	C^4	C^5	$C^{2'}$	$C^{4'}$	$C^{5'}$	CMe_2	other
1	129.8	169.0	139.5	130.7	159.8	69.1	79.6	29.2	
2	122.4	140.7	130.9	139.5	166.4	65.0	84.8	26.4	
4	126.2	136.3	134.7	165.3	164.3	68.3	80.3	29.2	
5	120.3	140.0	130.5	139.8	165.3	64.3	83.7	26.3	120.3 (CF_3SO_3)
6	135.9 (br s)	175.8 (d, J = 118.7)	137.1	127.4	161.3	67.8	79.4	28.6	134.8 (J = 13.8, C_{ortho}), 131.6 (J = 2.2, C_{para}), 131.4 (J = 51.0, C_{ipso}), 129.4 (J = 10.8, C_{meta})
7	125.9 (d, J = 6.6)	190.9 (d, J = 111.9)	137.9 (d, J = 8.1)	138.8	167.4	62.8	82.6	26.2	134.3 (J = 13.7, C_{ortho}), 131.9 (J = 2.3, C_{para}), 129.7 (J = 54.1, C_{ipso}), 129.3 (J = 11.2, C_{meta})
8	124.6	195.8	140.5	138.7	171.2	63.3	84.3	26.5	
9	127.1	136.7	129.3	127.1	165.2	69.8	81.4	28.9	

	C^2	C^3	C^4	C^5	$C^{2'}$	$C^{3'}$	$C^{4'}$	$C^{5'}$	$C^{6'}$	other
10	146.2	125.8	136.7	174.3 (J = 117.8)	154.2	119.1	135.0	121.0	149.7	134.7 (J = 18.7, C_{ortho}), 131.8 (J = 2.5, C_{para}), 130.8 (J = 51.0, C_{ipso}), 129.4 (J = 10.8, C_{meta})
11	132.7	134.7	136.0	182.4 (J = 122.1)	151.7	129.8	144.4	124.8	146.7	134.5 (J = 13.6, C_{ortho}), 131.8 (br s),131.3 (J = 70.0), 129.6 (J = 11.0), 48.2 (NMe)

[a] Chemical shifts are given in parts per million and coupling constants (J) in hertz.

Scheme 1



complex **3** could not, however, be isolated in a pure form or characterized satisfactorily as its yield was too low.

The (thienyl)oxazoline compound was also lithiated at C^5 with LDA at −80 °C. The addition of one or more molar amounts of [AuCl(tht)] to a solution of the thien-5-yllithium in THF (tetrahydrofuran) surprisingly also produced a neutral trimeric complex **4**, which was crystallised at room temperature from THF/diethyl ether using vapor diffusion methods (Scheme 2). The molecular structure of this 18-membered ring was determined by X-ray diffraction, but this will be reported elsewhere together with the results for an *ab initio* theoretical study. Burini *et al.* have previously postulated trimeric compounds for simple gold imidazolyls.[21,22] Protonation of complex **4** in the presence of triphenylphosphine afforded the (thienyl)oxazolium cation **5** (Scheme 2) and a homoleptic gold phosphine complex that was not further characterized. Complexes **1**, **2**, and **4** are thermally stable in air at room temperature and are soluble in methylene chloride, THF, and acetone.

It is clear that the neutral free (thienyl)oxazoline (7.56, H^3; 7.40 H^5; 7.03, H^4; 4.06, CH_2; 1.35, CMe_2) and the neutral gold compounds **1** and **4** (Table 1) have comparable proton chemical shifts, while the proton shifts of the cationic gold complexes **2** and **3** are similar to those of the cationic (thienyl)oxazolium compound **5**.

The ^{13}C chemical shifts of the coordinated carbon in the neutral heterometallacyclic complexes **1** and **4** (Table 2) occur at δ 169.0 and 165.3, respectively. They are shifted $\Delta\delta$ 38.9 and 35.9 ppm downfield relative to the corresponding carbons in free (thienyl)oxazoline (δ 130.1, C^3; 129.4, C^5).

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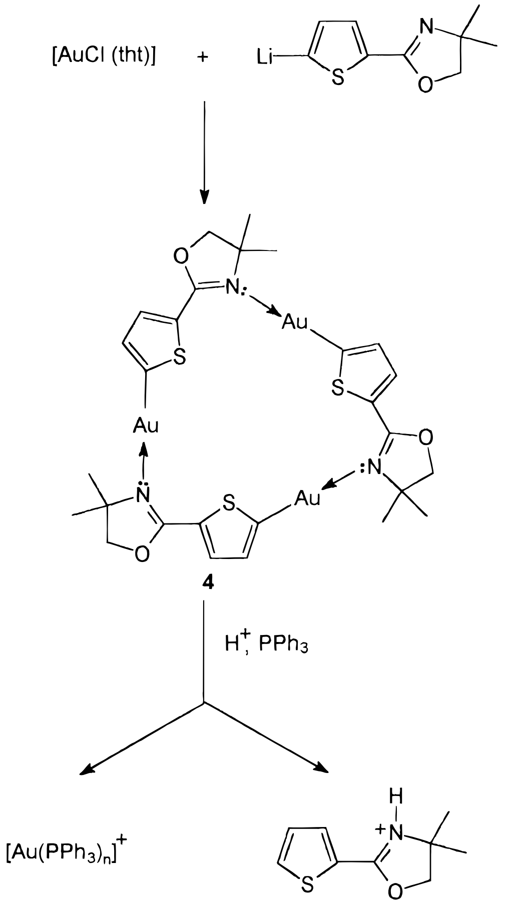
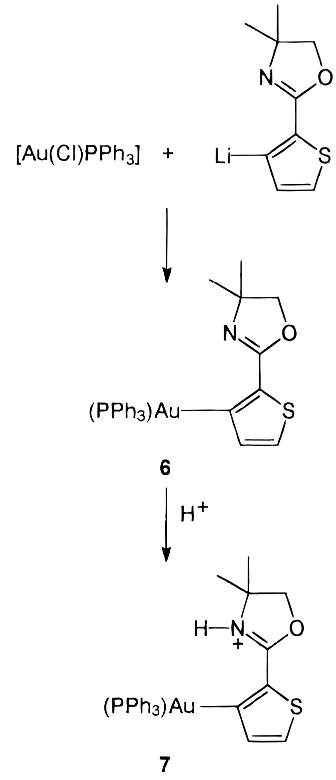
Scheme 2



Scheme 3



The carbon atom of the counterion $CF_3SO_3^-$ is not normally visible in $^{13}C\{^1H\}$ NMR spectra since the signal is split as a result of coupling to the fluorine atoms.[6–9] Interestingly, the quartet exhibited by this carbon is clearly observable in the spectrum of complex **5** (Table 2). This is probably due to the high solubility of this compound in the deuterated solvent, giving a very favorable concentration for higher resolution.

The molecular ion peak at *m/z* 754 is also the base peak in the mass spectrum of the dimeric complex **1**. The fragmentation pattern is not very complex, and *m/z* values corresponding to [dimer − Au]+, [monomer − Me]+, [(thienyl)oxazoline]+, and [(thienyl)oxazoline − Me]+ are observed. The complex cation in the nitrogen-coordinated complex **2** is observed at *m/z* 559. The dimerized thienyl(oxazoline) cation at *m/z* 360, the ionized (thienyl)oxazoline ligand at *m/z* 181, and the fragment [(thienyl)oxazoline − Me] at *m/z* 166 are also present for this complex.

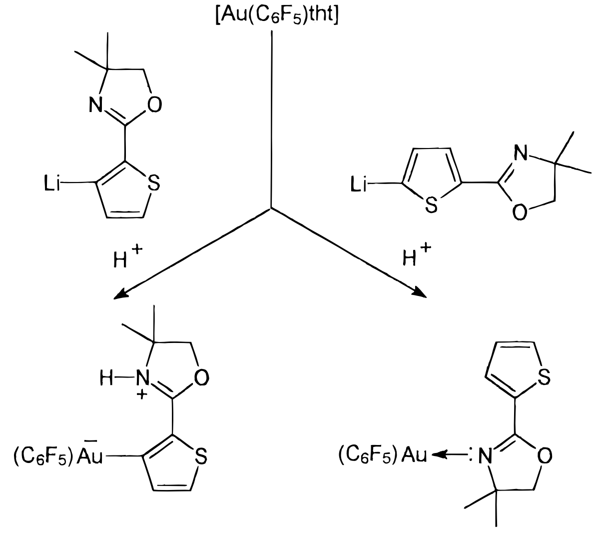
Neutral Phosphine-Containing 3-(Thienyl)oxazoline and Cationic Carbene Complexes of Gold. The neutral thienyl complex **6** was prepared by reacting $[AuCl(PPh_3)]$ with 2-(4′,5′-dihydro-4′,4′-dimethyloxazolin-2′-yl)thien-3-yllithium in diethyl ether at −80 °C (Scheme 3). The solvent was removed, and complex **6** was extracted with methylene chloride, filtered through Celite, and crystallized using vapor diffusion methods. Off-white, needle-like crystals were obtained.

Substitution of the phosphine occurs in the analogous neutral thiazolyl[6] and imidazolyl[9] gold complexes, which undergo dissociative polymerization. As mentioned earlier, Burini and co-workers have suggested that such polymeric compounds exist as cyclic trimers.[21,22] Interestingly, the (thienyl)oxazoline gold complex **6** does not oligomerize even though a very stable analogous dimer, complex **1** (Scheme 1), spontaneously forms in the reaction of [AuCl(tht)] with lithiated (thienyl)oxazoline. The mass spectrum of complex **6** does not exhibit a molecular ion, however, *m/z* values corresponding to the dimer and fragments thereof are observed, indicating that the expected reaction does occur in the mass spectrometer.

The neutral thienyl complex **6** was readily protonated with CF_3SO_3H in THF at −65 °C to form the cationic diorganocarbene complex **7** (Scheme 3). Crystallization from methylene chloride/diethyl ether afforded colorless needles of complex **7**. This diorganocarbene complex is unique in that its formation conclusively demonstrates that an α-heteroatom is not a requirement for stable gold carbene complexes. It also represents the first gold carbene complex obtained according to our methodology, which is derived from a precursor complex in which the nitrogen atom is located outside the coordinated ring system.

The $^{13}C\{^1H\}$ NMR data for the neutral complex **6** shows that the coordinated carbon resonates at δ 175.8 and that it is shifted downfield with respect to the corresponding carbon (C^3) of free (thienyl)oxazoline resonating at δ 130.1 ($\Delta\delta = 45.7$ ppm). This downfield shift is of the same order of magnitude as that shown by isothiazole/isothiazolyl ($\Delta\delta = 41.4$ ppm)[7] and 1-phenylpyrazole/pyrazolyl ($\Delta\delta = 45.1$ ppm) upon deprotonation and coordination. All of these shifts are much larger than those experienced by the same carbon atoms on coordination to the $CpFe(CO)_2$ cationic unit. Transmetalation reactions between azolyl compounds and $CpFe(CO)_2Cl$ complexes give neutral azolyl compounds.[23–25] Similar comparisons of the eventually coordinated carbon atom resonance before and after

Scheme 4



8 **9**

coordination in iron complexes show that for isothiazole/isothiazolyl[24] this difference is only Δ*δ* 14.1 ppm, for pyrazole/pyrazolyl it is Δ*δ* 18.6 ppm, for (thienyl)oxazoline/3-thienyl(oxazoline) it is Δ*δ* 19.6 ppm, and for (thienyl)oxazoline/3-thienyl(oxazoline) it is Δ*δ* 18.7 ppm.[25] The downfield shifts of Δ*δ* 38.9 and 35.9 ppm exhibited by complexes **1** and **4** are somewhat smaller than those occurring in triphenylphosphine gold compounds, but they are still much larger than those measured for cyclopentadienyl iron complexes. The difference in the $^{13}C\{^1H\}$ NMR chemical shifts of the coordinated carbon in the precursor neutral complex **6** and the cationic diorganocarbene complex **7** is Δ*δ* 15.1 ppm. This is large compared to the Δ*δ* 5.4 ppm obtained previously for the corresponding isothiazolyl/isothiazolinylidene gold phosphine complexes.[7] It is not possible to compare the corresponding chemical shift difference in the thiazolyl/thiazolinylidene[6] and imidazolyl/imidazolinylidene[9] systems due to complicating reactions, such as polymerization and homoleptic rearrangement, which prevent the isolation of the carbene complexes.

A Neutral Diorganocarbene Complex and a Nitrogen-Coordinated Complex of Pentafluorophenylgold. The neutral (thienyl)oxazolinyl monocarbene complex **8** was prepared by treating $[Au(C_6F_5)(tht)]$ with (thienyl)oxazoline lithiated at C^3 in diethyl ether followed by direct protonation at −60 °C of the intermediately formed aurate complex with CF_3SO_3H (Scheme 4). The white precipitate was collected, washed several times with diethyl ether, redissolved in methylene chloride, and filtered through Celite. Crystallization afforded colorless, needle-like crystals of complex **8**.

The diorganocarbene complex **8**, unlike the analogous thiazolinylidene, isothiazolinylidene, pyrazolinylidene, and imidazolinylidene complexes, does not undergo homoleptic rearrangement in solution.[6−9] It is also the first diorganocarbene complex of gold to be synthesized.

The neutral nitrogen-coordinated pentafluorophenylgold complex **9** resulted from sequential treatment of $[Au(C_6F_5)(tht)]$ with the (thienyl)oxazoline compound lithiated at C^5 with LDA at −70 °C and CF_3SO_3H (Scheme 4). The solvent was removed under vacuum, and complex **9** was extracted with diethyl ether before filtration through Celite. Crystallization from diethyl ether/pentane afforded off-white crystals of complex **9**. The expected monocarbene complex was not obtained. The well-established lability of bicovalent sulfur-donor complexes of gold(I) and gold(III),[26] the stability of the gold−imine linkage in various compounds,[27−30] as well as the clear preference of gold(I) for the nitrogen atom in the ligand $[\mathrm{MeS}\overline{\mathrm{C{=}NCMe{=}CHS}}]$,[31] led us to postulate the formation of nitrogen- rather than sulfur-coordinated products **2** and **9**.

Complex **8** is only soluble in THF, while complex **9** is soluble in diethyl ether and most other polar organic solvents. Both compounds are stable in solution in air for a limited period only.

The ^1H NMR data of the neutral diorganocarbene complex **8** and the cationic diorganocarbene complex **7** are surprisingly similar. The H^4, H^5, and Me protons have essentially the same chemical shifts, while the CH_2 resonances differ by only 0.2 ppm. Usually a decrease in positive charge is accompanied by an upfield shift of the proton resonances. One is tempted to ascribe the unexpected downfield position of the protons of the neutral complex **8** to the deshielding effect of the C_6F_5 group. However, if this was the case, then the proton chemical shifts of the neutral nitrogen-coordinated complex **9**, which also contains a C_6F_5 group, should also appear at a more downfield position to make them comparable to those in the cationic diimine complex **2** (Scheme 1). This, however, is not true. As expected, the proton resonances of the latter complex **2** lie far downfield from those of the neutral complex **9**. The similarity of the ^1H NMR chemical shifts in the two carbene complexes **7** and **8** suggests that the electronic distribution in the framework of the two compounds is very similar and probably implies that complex **8** contains a dominant resonance structure in which there is a negative charge located mainly on the Au as well as an equal but positive charge located mainly on the nitrogen atom. In **7**, the situation in the ring system is identical but the gold itself is approximately neutral.

In the $^{13}C\{^1H\}$ NMR spectra of complexes **8** and **9**, the signals of the C_6F_5 ligand are very weak and are partly visible as a series of multiplets due to coupling of the ^{19}F nuclei with the carbon nuclei. The ^{13}C chemical shifts of the neutral and cationic carbene complexes **7** and **8** are once again very similar. The carbene carbon of complex **8**, however, resonates at a somewhat lower field than that of the cationic carbene complex, similar to the situation found in thiazolinylidene, imidazolinylidene, and isothiazolinylidene cationic and neutral compounds.[6−9]

Since the compounds are isomeric, the same molecular ion peak at *m/z* 545 was observed for both

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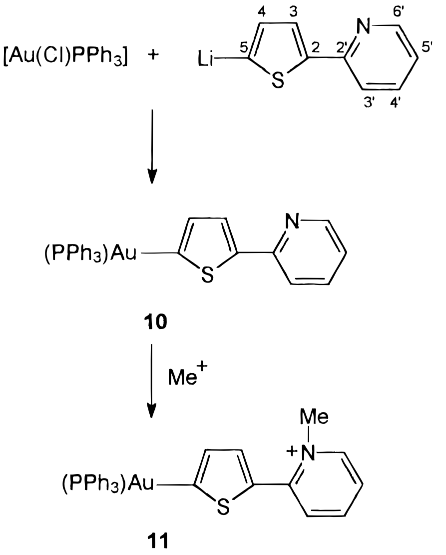
Scheme 5



compounds **8** and **9**. The fragmentation patterns of complex **8** consist of the loss of either the (thienyl)oxazoline ligand or the C_6F_5 ligand while that of complex **9** only shows the loss of the (thienyl)oxazoline ligand. The fragment [(thienyl)oxazoline − Me]$^+$ at m/z 166 forms the base peak in both spectra.

Neutral (Thienyl)pyridyl and (Thienyl)pyridinylidene Complexes of (Triphenylphosphine)gold. The reaction of 1 molar equiv of 2-(2′-pyridyl)thien-5-yllithium with [AuCl(PPh$_3$)] at −40 °C afforded the neutral thienyl gold complex **10** (Scheme 5). The solvent was removed under vacuum, and the residue was extracted with methylene chloride before filtration through Celite. Crystallization from methylene chloride/hexane afforded yellow crystals of complex **10**.

Alkylation of the thienyl complex **10**, at 0 °C with CF_3SO_3Me followed by crystallization from methylene chloride/hexane, produced orange blocks of the cationic organothio carbene complex **11** (Scheme 5). This synthesis, like that of **6** and **7**, was not complicated by homoleptic rearrangement or polymerization.

The cationic compound is only slightly soluble in diethyl ether, while both compounds readily dissolve in acetone, methylene chloride, and THF.

The ^{1}H NMR data of the neutral complex **10** show that the resonances of the protons of the thienyl ring are similar to those of free 2′-(2-thienyl)pyridine (δ 7.72, H^3; 7.13, H^4), while the proton resonances of the pyridyl ring are shifted slightly downfield with respect to those of 2′-(2-thienyl)pyridine (δ 7.79, H^3; 7.81, H$^{4'}$; 7.22, H$^{5'}$; 8.52, H$^{6'}$). Yet again, the proton resonances of the neutral complex **10** are comparable to those of free 2′-(2-thienyl)pyridine, while the resonances of complex **11** resemble those of the cationic 2′-(2-thienyl)pyridinium compound (δ 8.21, H^3; 7.34, H^4; 8.06, H$^{3'}$; 8.42, H$^{4'}$; 7.76, H$^{5'}$; 8.82, H$^{6'}$). The H$^{3'}$ and H$^{4'}$ proton signals of complex **10** lie under the multiplet of the phenyl ring.

The ^{13}C resonance of the coordinated carbon of the thienyl ring of compound **10** appears at δ 174.3 and is shifted $\Delta\delta$ 45.5 ppm downfield with respect to C^5 of the free (thienyl)pyridine. This downfield shift is similar to those discussed previously upon formation of the corresponding isothiazolyl complex ($\Delta\delta$ = 41.4)[7] and (thienyl)oxazoline complex **6** ($\Delta\delta$ = 45.7). The ^{13}C resonance of the carbene carbon of complex **11** has a chemical shift of δ 182.4; this however is not surprising, and the downfield shift of $\Delta\delta$ 8.1 ppm compares to the 5.4 ppm downfield shift observed when the isothiazolyl complex changes to the isothiazolinylidene complex.[7]

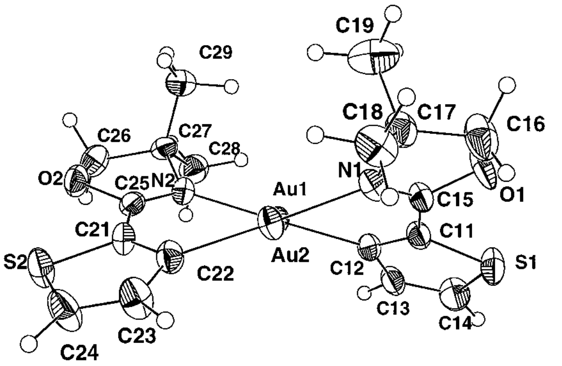


Figure 1. The molecular structure of complex **1**. The thermal ellipsoids are drawn at 50% probability limit.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg), with Esd in Parentheses, for Complex 1

Au1−Au2	2.8450(6)		
Au1−N2	2.065(8)	Au2−N1	2.091(8)
Au1−C12	2.01(1)	Au2−C22	2.04(1)
S1−C11	1.73(1)	S2−C21	1.72(1)
S1−C14	1.71(1)	S2−C24	1.71(1)
O1−C15	1.35(1)	O2−C25	1.36(1)
O1−C16	1.44(1)	O2−C26	1.47(1)
N1−C15	1.28(1)	N2−C25	1.30(1)
N1−C17	1.51(1)	N2−C27	1.53(1)
C11−C12	1.37(1)	C21−C22	1.39(1)
C11−C15	1.46(1)	C21−C25	1.45(1)
C12−C13	1.40(1)	C22−C23	1.39(1)
C13−C14	1.36(2)	C23−C24	1.36(2)
C16−C17	1.51(2)	C26−C27	1.51(2)
C17−C18	1.54(2)	C27−C28	1.53(1)
C17−C19	1.53(2)	C27−C29	1.49(1)
Au2−Au1−N2	90.3(2)	Au2−Au1−C12	94.0(3)
N2−Au1−C12	175.6(3)	N1−Au2−C22	175.9(3)
Au1−Au2−N1	89.4(2)	Au1−Au2−C22	94.3(3)
C11−S1−C14	90.8(5)	C21−S2−C24	91.6(5)
Au2−N1−C15	129.7(6)	Au2−N1−C17	123.0(7)
Au1−N2−C25	130.2(7)	Au1−N2−C27	120.3(6)
Au1−C12−C11	126.2(7)	Au1−C12−C13	124.0(7)
C11−C12−C13	109.8(9)	C21−C22−C23	110.1(9)
Au2−C22−C21	124.5(8)	Au2−C22−C23	125.2(8)

Structure of $[Au\{C{=}C(C{=}NCMe_2CH_2O)SCH{=}CH\}]_2$, 1. The molecular structure of complex **1** is shown in Figure 1. Selected bond lengths and bond angles are given in Table 3. The crystallographic data discussed below refer to the numbering scheme adopted in Figure 1.

Each gold atom is essentially linearly coordinated to a carbon atom of a 4′,5′-dihydro-4′,4′-dimethyl-2′-(2-thienyl)oxazoline ligand and the nitrogen atom of a second (thienyl)oxazoline ligand to form a cyclic binuclear Au(I) compound. This is the only structure of a C,N-coordinated six-membered edge-sharing (Au−Au) bicyclic compound known. No intermolecular Au···Au interactions occur; however, the gold atoms within the bicyclic compound are intramolecularly bound and exhibit a short separation of 2.8450(6) Å.

The two ligands of the dimeric complex **1** are not coplanar, and the N-donor and C-donor units are rotated with respect to each other to give N−Au−Au−C dihedral angles of 35.8(4)° and 36.8(4)°. There are two possible reasons for this buckling (distortions that

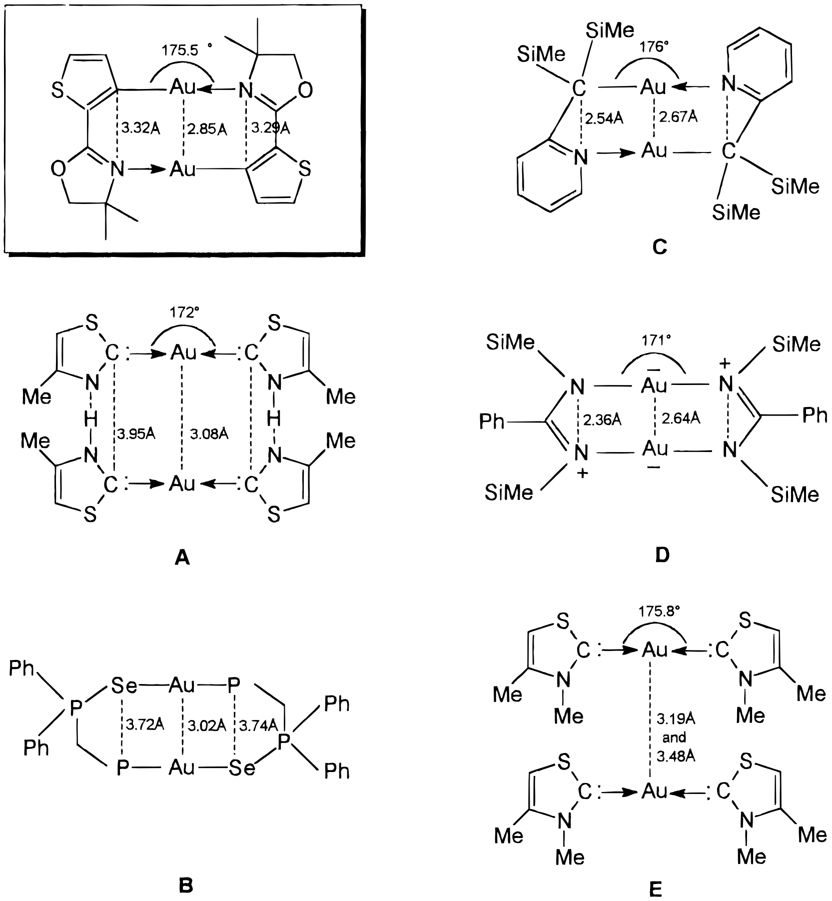


Figure 2. Representative six- and five-edge-sharing (Au–Au) bicyclic compounds.

destroy the coplanarity of the two ligands). Firstly, the rotation reduces cyclic strain (if the ring does not buckle then the system is strained), and secondly, it brings the Au atoms closer together, encouraging the formation of stronger Au···Au interactions

A search of the Cambridge data base[32] revealed that all six-membered edge-sharing (Au–Au) bicylic ring systems are buckled with dihedral angles varying from 26.54(8) to 83.23(8)°, whereas similar five-membered ring systems are generally not buckled or only slightly so. They mostly contain dihedral angles ranging from 0 to 5°. Some structural information on binuclear complexes related to complex **1** are collected in Figure 2. It is evident that this type of ring twisting occurs in compounds **A**,[6] **B**,[33] and **D**[34] (Figure 2) with dihedral angles of 64.8(4)°, 48.12(6)°, and 15.61(3)°, respectively. In compound **D** (Figure 2),[34] the two rings are twisted even though no cyclic strain is evident. It is possible, therefore, that the two rings only twist to bring the gold atoms closer together. It contains a very short Au···Au contact of 2.64(6) Å. Compound **C**,[29] which is also a five-membered edge-sharing bicyclic compound, is not twisted, probably due to the steric constraints caused by two $SiMe_3$ groups on each coordinated carbon atom. Surprisingly, however, the short Au···Au contact distance of 2.67(2) Å is longer than the coordinated carbon–nitrogen contact distance of 2.535 Å. The Au···Au bond seems to cause the C–Au–N angles to "bulge" outwards.

Six membered edge-sharing (Au–Au) bicyclics, like those in compounds **A** and **B** and compound **1** (Figure 2), generally display longer Au···Au separations than comparable five-membered rings. Further investigations using the Cambridge database revealed that typical Au···Au bond distances in such six-membered rings fall within the range 2.83–3.24 Å, with a mean value of 3.02 Å, and gold atoms in five-membered rings are separated by distances of 2.55–3.17 Å, with a mean value of 2.76 Å.[32] Complex **1**, therefore, contains an uncommonly short Au···Au bond for a six-membered ring. Indeed, only one six-membered ring gold compound exists with a shorter Au···Au distance, and it is a P,P-chelate within a Au–Ru cluster.[35] Compound **E**,[36] which does not form a binuclear ring structure, forms intermolecular Au···Au bonds of comparable lengths to those compounds of **A** and **B**. The C–Au–C units are also rotated with respect to one another to form a torsional angle of 110.9(7)°.

Coordination around the two central gold atoms in complex **1** is somewhat distorted from linearity (C–Au–N angles of 175.5(9)° and 173.8(8)°), but as depicted in Figure 2, this is not uncommon for Au(I) compounds.

The Au–C(sp^2) bond lengths of 2.07(3) and 2.04(3) Å are in agreement with those found in other neutral gold(I) complexes, e.g., compound **A** (Figure 2) (average

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2.03(1) Å),[6] $[Au\{C{=}CHCH{=}NS\}PPh_3]$ (2.032(7) Å),[7] $[Au(C_6F_5)PPh_3]$ (2.063(2) Å),[37] and compound **C** (Figure 2) (2.09(3) Å).[29]

The Au−N(imine) distances, with lengths of 2.065(8) and 2.091(9) Å, are normal and compare well with similar distances in, for example, compound **C** (2.08 Å)[21] and compound **D** (average 2.06 Å).[34]

The aromatic character of the two thienyl rings is clearly shown by the planarity of the rings (maximum deviation from least squares plane of 0.0017 and 0.0223 Å) and the relatively short C−C (average 1.37(1) Å) and C−S (average 1.72(1) Å) bond lengths therein. In addition, the bonds joining the thienyl and oxazolinyl rings, C11−C15 and C21−C25 (average 1.46(1) Å), are also shorter than normal single C−C bond lengths. C21, C22, C25, and N2 all lie in the same plane with a maximum deviation from the least squares plane of 0.0595 Å, while C11, C12, C15, and N1 are somewhat less planar (maximum deviation from the least-squares plane of 0.10 Å). All these results indicate that π-delocalization occurs in complex **1**.

Conclusion

Unique 6-membered dimeric and 18-membered trimeric thienyl gold compounds as well as divinyl- and organothiocarbene complexes have been isolated. The divinylcarbene complexes **7** and **8** as well as the organothiocarbene complex **11** exhibit a characteristic low-field chemical shift for the coordinated carbon. The C^3 carbon atom of the thienyl(oxazoline) ligand resonates between δ 136.7 and 140.7 when an imine compound is formed; it resonates between δ 169.0 and 175.8 when it is coordinated to gold and between δ 190.9 and 195.8 upon carbene complex formation. It is, thus, evident that the coordinated carbon atom is effected during alkylation and carbene complex formation. The carbene complexes have been represented with a positive charge on the nitrogen atom, as this is believed to be the dominant resonance form. This method of representation, however, belies the fact that a characteristic low-field chemical shift for the carbene carbon atom is obtained.

Experimental Section

General Comments. All reactions involving organometallic reagents were performed under an atmosphere of nitrogen using standard vacuum line and Schlenk techniques. Melting points were determined on a standardized Buchi 535 apparatus. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument at *ca.* 70 eV and NMR spectra on a Varian 200 FT spectrometer. Elemental analyses were carried out by the Division of Energy Technology, Council for Scientific and Industrial Research, Pretoria, South Africa.

Reagents. The following starting materials were prepared according to published procedures: 4′,4′-dimethyl-2′-(2-thienyl)-2′-oxazoline,[10] 2′-(2-thienyl)pyridine,[38] [AuCl(tht)], [AuCl(PPh$_3$)], and $[Au(C_6F_5)(tht)]$.[26] CF_3SO_3Me and CF_3SO_3H were purchased from Aldrich and *n*-butyllithium from Merck. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen from sodium diphenylketyl and CH_2Cl_2, hexane and pentane were distilled from CaH_2.

Preparation of $[Au\{C{=}C(C{=}NCMe_2CH_2O)SCH{=}CH\}]_2$ (1). A solution of 4′,4′-dimethyl-2′-(2−thienyl)-2′-oxazoline (0.18 g, 1.00 mmol) in diethyl ether was cooled to −80 °C and treated with standardized *n*-butyllithium in hexane (0.63 cm^3, 1.00 mmol, 1.6 M). The light yellow solution was stirred at −80 °C for 20 min and at −10 °C for 30 min. A solution of [AuCl(tht)] (0.32 g, 1.00 mmol) in THF (50 cm^3) was added dropwise at −60 °C. The mixture was stirred at −60 °C for 1 h and at −10 °C for 30 min before allowing it to warm up to room temperature. The solvent was removed under vacuum. The residue was washed several times with diethyl ether, redissolved in THF, and filtered through Celite. Concentration of the yellow filtrate, slow addition of diethyl ether, and cooling to −20 °C afforded yellow crystals of complex **1**. Yield 63.9%, mp > 155 °C (dec). Anal. Calcd for $C_{18}H_{20}Au_2N_2O_2S_2$: C, 28.66; H, 2.67; N, 3.71. Found: C, 28.7; H, 2.5; N, 3.7.

Preparation of $[Au\{N{=}C(C{=}CHCH{=}CHS)OCH_2CMe_2\}_2][CF_3SO_3]$ (2). A solution of 4′,4′-dimethyl-2′-(2-thienyl)-2′-oxazoline (0.37 g, 2.02 mmol) in diethyl ether was cooled to −80 °C and treated with standardized *n*-butyllithium in hexane (1.26 cm^3, 2.02 mmol, 1.6 M). The light yellow solution was stirred at −80 °C for 20 min and at −10 °C for 30 min. A solution of [AuCl(tht)] (0.32 g, 1.00 mmol) in THF (50 cm^3) was added dropwise at −60 °C. The mixture was stirred at −60 °C for 2 h before the addition of CF_3SO_3H (0.18 cm^3, 2.02 mmol). The reaction mixture was allowed to stir at this temperature for 2 h and at −45 °C for 2 h before warming to room temperature. The solvent was removed *in vacuo*, and the yellow residue was washed several times with diethyl ether, redissolved in CH_2Cl_2, and filtered through Celite. Concentration of the light yellow filtrate, slow addition of pentane, and cooling to −20 °C afforded yellow crystals of complex **2**. Yield 40.4%, mp > 96 °C. Anal. Calcd for $C_{19}H_{22}AuF_3N_2O_5S_3$: C, 32.21; H, 3.13; N, 3.95. Found: C, 32.1; H, 3.1; N, 4.1.

Preparation of $[Au\{C{=}CHCH{=}C(C{=}NCMe_2CH_2O)S\}]_3$ (4). A solution of 4′,4′-dimethyl-2′-(2-thienyl)-2′-oxazoline (0.28 g, 1.52 mmol) in THF was slowly added to a solution of LDA, prepared from diisopropylamine (0.22 cm3, 1.58 mmol) and standardized *n*-butyllithium in hexane (1.00 cm^3, 1.60 mmol, 1.6 M), at −78 °C. The solution was stirred at −80 °C for 30 min before [AuCl(tht)] (0.48 g, 1.50 mmol) was added at −78 °C. The mixture was stirred for 30 min at −80 °C, 1 h at −50 °C, and 30 min at room temperature. The solvent was removed *in vacuo*, and the residue was washed several times with diethyl ether and redissolved in CH_2Cl_2. Filtration through Celite, concentration of the yellow filtrate, slow addition of diethyl ether, and cooling to −20 °C afforded yellow crystals of complex **4**. Yield 72.3%, mp > 134 °C (dec). Anal. Calcd for $C_{27}H_{30}Au_3N_3O_3S_3$: C, 28.66; H, 2.67; N, 3.71. Found: C, 28.7; H, 2.5; N, 3.8.

Preparation of $[Au\{C{=}C(C{=}NCMe_2CH_2O)SCH{=}CH\}PPh_3]$ (6). A solution of 4′,4′-dimethyl-2′-(2-thienyl)-2′-oxazoline (0.22 g, 1.20 mmol) in diethyl ether was cooled to −80 °C and treated with standardized *n*-butyllithium in hexane (0.78 cm^3, 1.25 mmol, 1.6 M). The light yellow solution was stirred at −80 °C for 20 min and at −10 °C for 30 min before [AuCl(PPh$_3$)] (0.50g, 1.00 mmol) was added at −5 °C. The mixture was stirred for 30 min at −5 °C, and THF (20 cm^3) was added. The reaction mixture was stirred at −5 °C for a further 2 h and allowed to warm to room temperature before the solvent was removed. The residue was washed once with diethyl ether, redissolved in CH_2Cl_2, and filtered through Celite. Concentration of the colorless filtrate, slow addition of hexane, and cooling to −20 °C afforded colorless crystals of complex **6**. Yield 86.0%, mp 173 °C. Anal. Calcd for $C_{27}H_{25}AuNOPS$: C, 50.71; H, 3.94; N, 2.19. Found: C, 50.7; H, 3.8; N, 2.2.

Preparation of $[Au\{CC{=}(CN(H)CMe_2CH_2O)SCH{=}CH\}PPh_3][CF_3SO_3]$ (7). A solution of complex **6** (0.93 g, 1.45 mmol) in THF was cooled to −65 °C and treated dropwise with CF_3SO_3H (0.13 cm^3, 1.45 mmol). The mixture was stirred for

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Table 4. Crystal Data, Collection, and Refinement Details for Complex 1

formula	$C_{18}H_{20}Au_2N_2O_2S_2$
cryst size, mm	0.26 × 0.12 × 0.11
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	9.1976(15)
b, Å	17.8049(14)
c, Å	12.6733(18)
α, deg	90
β, deg	100.507(13)
γ, deg	90
Z	4
V, Å^3	2040.6(5)
d_c, g·cm^{-3}	2.456
μ, mm^{-1}	14.03
radiation	Mo Kα (0.710 73 Å)
temp, °C	25
F(000)	1192
diffractometer	Enraf-Nonius CAD 4
scan type	$\omega-2\theta$
scan range, *θ*, deg	$2 \leq \theta \leq 25$
hkl ranges	−10 to 10, 0−21, 0−15
max scan rate, deg min^{-1}	5.5
max scan time per refln, s	60
no. of reflns measd	3567
no. of unique reflns used	2777
no. of params refined	235
goodness of fit	2.196
R, *R′*	0.027, 0.057

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R' = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2$.

1 h at this temperature before warming to room temperature. The solvent was removed *in vacuo*, and the residue was washed several times with diethyl ether, redissolved in CH_2Cl_2, and filtered through Celite. Concentration of the colorless filtrate, slow addition of diethyl ether, and cooling to −20 °C afforded colorless crystals of complex **7**. Yield 49.7%, mp 126−127 °C. Anal. Calcd for $C_{28}H_{26}AuF_3NO_4PS_2$: C, 42.59; H, 3.28; N, 1.77. Found: C, 42.4; H, 3.3; N, 1.8.

Preparation of [Au(C_6F_5){CC=(CN(H)CMe$_2$CH$_2$O)SCH=CH}] (8). A solution of 4′,4′-dimethyl-2′-(2-thienyl)-2′-oxazoline (0.18 g, 1.00 mmol) in diethyl ether was cooled to −80 °C and treated with standardized *n*-butyllithium in hexane (0.63 cm^3, 1.00 mmol, 1.6 M). The light yellow solution was stirred at −80 °C for 20 min and at −10 °C for 30 min before [Au(C_6F_5)(tht)] (0.45g, 1.00 mmol) was added at −75 °C. The mixture was stirred for 1 h at −80 °C and for 45 min at −60 °C before the addition of CF_3SO_3H (0.10 cm^3, 1.00 mmol). The reaction mixture was allowed to stir at this temperature for 1 h before warming to room temperature. The white precipitate was collected and washed several times with diethyl ether, redissolved in CH_2Cl_2, and filtered through Celite. Concentration of the colorless filtrate, slow addition of diethyl ether, and cooling to −20 °C afforded colorless needle-like crystals of complex **8**. Yield 92.1%, mp > 170 °C (dec). Anal. Calcd for $C_{15}H_{11}AuF_5NOS$: C, 33.04; H, 2.03; N, 2.57. Found: C, 32.9; H, 1.9; N, 2.5.

Preparation of [Au(C_6F_5){N=C(C=CHCH=CHS)OCH$_2$CMe$_2$}] (9). A solution of 4′,4′-dimethyl-2′-(2-thienyl)-2′-oxazoline (0.19 g, 1.05 mmol) in THF was slowly added to a solution of LDA, prepared from diisopropylamine (0.15 cm^3, 1.06 mmol) and standardized *n*-butyllithium in hexane (0.67 cm^3, 1.07 mmol, 1.6 M) at −70 °C. The reaction mixture was allowed to stir at this temperature for 1 h, before [Au(C_6F_5)(tht)] (0.45g, 1.00 mmol) was added at −70 °C. The mixture was stirred for 1 h at −70 °C and at −50 °C for 1 h before the addition of CF_3SO_3H (0.10 cm^3, 1.00 mmol). The reaction mixture was allowed to stir at this temperature for 1 h before warming to room temperature. The solvent was removed in *vacuo*, and the oily residue was redissolved in diethyl ether and filtered through Celite. Concentration of the colorless filtrate, slow addition of pentane, and cooling to −20 °C afforded off-white crystals of complex **9**. Yield 89.6%, mp > 97 °C (dec). Anal. Calcd for $C_{15}H_{11}AuF_5NOS$: C, 33.04; H, 2.03; N, 2.57. Found: C, 33.1; H, 2.1; N, 2.4.

Preparation of [Au{C=CHCH=C(C=NCH=CH-CH=CH)S}PPh$_3$] (10). A solution of 2′-(2-thienyl)pyridine (0.24 g, 1.49 mmol) in THF was cooled to −5 °C and treated with standardized *n*-butyllithium in hexane (0.94 cm^3, 1.50 mmol, 1.6 M). The solution was stirred at −5 °C for 40 min before [AuCl(PPh$_3$)] (0.64 g, 1.29 mmol) was added at −40 °C. The mixture was stirred for 40 min at −40 °C and at room temperature for 30 min before the solvent was removed. The residue was washed once with ether, redissolved in CH_2Cl_2, and filtered through Celite. Concentration of the colorless filtrate, slow addition of hexane, and cooling to −20 °C afforded yellow crystals of complex **10**. Yield 55.8%, mp > 158 °C (dec). Anal. Calcd for $C_{27}H_{21}AuNPS$: C, 52.35; H, 3.42; N, 2.26. Found: C, 52.2; H, 3.5; N, 2.3.

Preparation of [Au{C=CHCH=C(C=N(Me)CH=CH-CH=CH)S}PPh$_3$][CF$_3$SO$_3$] (11). A solution of complex **10** (0.70 g, 1.13 mmol) in CH_2Cl_2 was cooled to 0 °C and treated with CF_3SO_3Me (0.13 cm^3, 1.13 mmol). The solution was stirred at this temperature for 45 min and at room temperature for 1 h. The solvent was removed *in vacuo*, and the residue was washed several times with diethyl ether. The residue was redissolved in CH_2Cl_2 and filtered through Celite. Concentration of the yellow filtrate, slow addition of hexane, and cooling to −20 °C afforded orange blocks of complex **11**. Yield 45.90%, mp > 150 °C (dec). Anal. Calcd for $C_{29}H_{24}AuF_3NO_3PS_2$: C, 44.45; H, 3.09; N, 1.79. Found: C, 44.5; H, 3.0; N, 1.9.

X-ray Crystallography for Complex 1. A yellow crystal of **1** was mounted on a glass fiber and transferred onto the diffractometer (Enraf-Nonius CAD4F). Data were collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) to $2\theta_{max} = 30°$ and corrected for Lorentz and polarization effects and for absorption using the Ψ-scan method. Unique sets of data with $I \geq 3.0\sigma(I)$ were used to solve the structure of **1** by the heavy-atom method, placing two gold atoms initially. The rest of the non-H atoms could be found from difference maps and their positions refined with weighted least-squares refinement. All non-H atoms were eventually refined with anisotropic displacement parameters. The positions of only some of the H atoms could be found from difference maps. Their positions were, therefore, calculated in ideal positions. In the final cycles of refinement, the H atoms were included with equal and constant isotropic displacement parameters and no positional parameters were refined. For structure solution and refinement, the XTAL 3.4[39] package was used while the H positions were calculated with Shelx76.[40] Important crystallographic parameters are given in Table 4.

Supporting Information Available: Tables of atomic coordinates, bond distances, contact distances, bond angles, and dihedral angles (6 pages). Ordering information is given on any current masthead page.

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(39) Hall, S. R.; King, G. S. D.; Stewart, J. M. *XTAL 34 Reference Manual*; Universities of Western Australia: Perth, 1995.

(40) Sheldrick, G. M. *Program for Crystal Structure Determination*; University of Cambridge: England, 1978.