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Ring opening reactions of thiiranes by alkoxo- and aryloxo-gold(I) complexes

Yoko Usui, Junko Noma, Masafumi Hirano and Sanshiro Komiya *

Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan. E-mail: komiya@cc.tuat.ac.jp; Fax: +81-42-387-7500

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Alkoxo- and aryloxo-gold(I) complexes [Au(OR)L] [R = $CH(CF_3)_2$, L = PPh_3 **1a** or PCy_3 **1b**; R = Ph, L = PPh_3 **1c**, PCy_3 **1d** or PMe_3 **1e**] smoothly reacted with ethylene sulfide to give the corresponding 2-(alkoxy- or -aryloxy)ethylsulfanylgold(I) complexes [Au(SCH_2CH_2OR)L] **2** at room temperature. Similar treatments of **1a**–**1e** with propylene sulfide, isobutylene sulfide, or styrene sulfide selectively cleaved the less hindered C–S bond of thiiranes to give corresponding 2-(alkoxy- or -aryloxy)ethylsulfanylgold(I) complexes. Reactions of **1a** with *cis*- and *trans*-2-butene sulfide gave *syn*- and *anti*-[Au(SCHMeCHMeOR)L], respectively, suggesting a mechanism involving an S_N2 type *trans* addition of alkoxogold(I) complexes toward thiiranes.

Introduction

Alkoxo and aryloxo complexes of late transition metals have received much attention because of their intrinsic ability as tools in both stoichiometric and catalytic chemical transformation.[1] While the metal–oxygen bonds in early transition-metal complexes are quite robust, those in late transition-metal complexes are generally weak leading to high nucleophilicity of their alkoxo and aryloxo ligands.[2] Among these alkoxo and aryloxo complexes of late transition metals, gold complexes were less explored to date. We have reported syntheses and chemical reactions of alkoxo- and aryloxo-gold-(I) and -(III) complexes which are highly basic showing hydrogen bonding with free alcohol,[3] hydrogen abstraction from active methylene compounds,[4] and transition metal hydrides[5] to give corresponding alkyl and heterodinuclear gold complexes. These gold complexes were also found to catalyse Knöevenagel reactions of aryl aldehydes with active methylene compounds under neutral and ambient conditions.[6] As an extension of our continuous study on alkoxogold complexes, we focused on the reactions with thiiranes. Thiiranes are considered to be versatile starting chemicals toward various sulfur containing compounds[7] and are known to be polymerised by Lewis acids and bases such as $TiCl_4$ and KOH,[7] and are desulfurised by tertiary phosphines[8] as well as by heating.[9] Ring opening reactions of thiiranes by primary alcohols are also known to be catalysed by BF_3 giving 2-alkoxyethanethiols,[10] though their yields and regio- and stereo-selectivities are poor. Although reactions of transition-metal complexes with thiiranes have also been extensively studied for desulfurisation,[11] the introduction of a sulfur atom into the complex,[12] formation of a thiametallacycle,[13] and cyclooligomerisation,[14] reactions of alkoxo and aryloxo complexes of transition metals with thiiranes are still unexplored so far. In this paper we report the regio- and stereo-selective ring opening reactions of thiiranes by alkoxo- and aryloxo-gold(I) complexes.

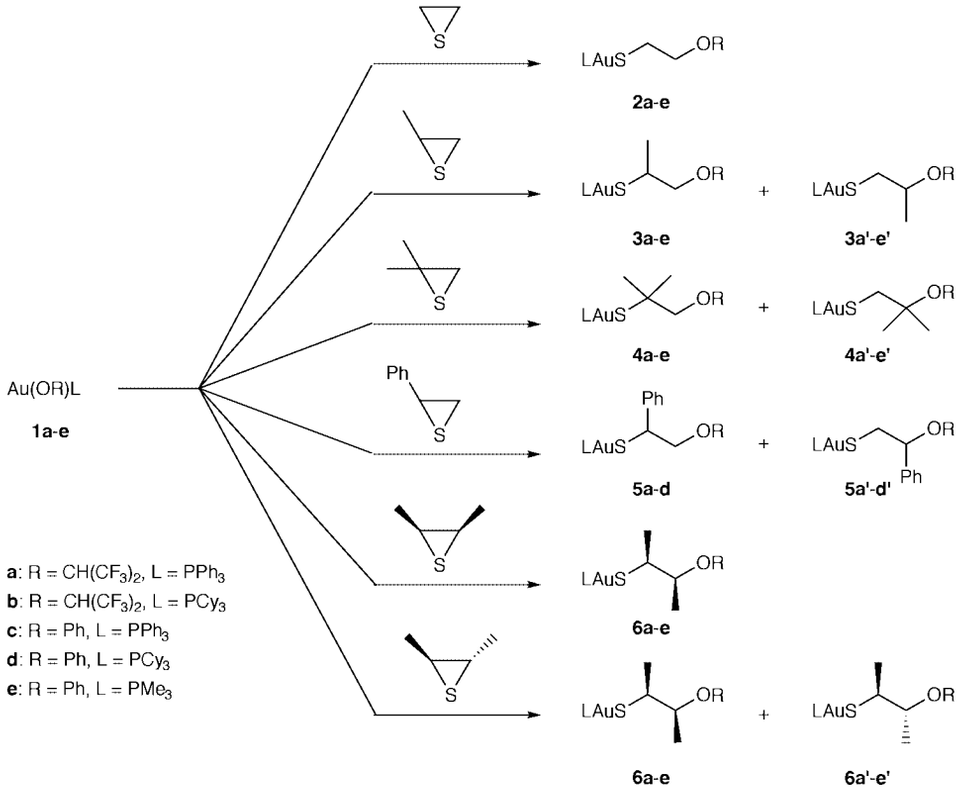
Results and discussion

Ring opening reaction of thiiranes by alkoxo- and aryloxo-gold(I) complexes

The reaction of the (1,1,1,3,3,3-hexafluoro-2-propoxo)gold(I) complex [Au{$OCH(CF_3)_2$}(PPh_3)] **1a** with ethylene sulfide at room temperature resulted in ring opening giving the novel [2-(1,1,1,3,3,3-hexafluoro-2-propoxy)ethylsulfanyl]gold(I) complex [Au{$SC_2H_4OCH(CF_3)_2$}(PPh_3)] **2a** in 66% yield. Results of the reactions of alkoxo- and aryloxo-gold(I) complexes with various thiiranes are summarised in Scheme 1 and Table 1.

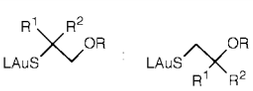
The A_2X_2 pattern at δ 3.46 (t, $J_{H\text{-}H}$ = 7.9 Hz, 2 H) and 4.02 (t, $J_{H\text{-}H}$ = 7.9 Hz, 2 H) in the ^{1}H NMR spectrum of complex **2a** shows the presence of a couple of magnetically inequivalent methylene groups suggesting cleavage of a C–S bond of ethylene sulfide. A septet at δ 3.42 (sep, $J_{H\text{-}F}$ = 6.6 Hz, 1 H) is assignable to the methine proton coupled to six equivalent fluorine nuclei of the 1,1,1,3,3,3-hexafluoro-2-propoxy group. A singlet at δ 36.8 in the ^{31}P-{^{1}H} NMR spectrum and multiplets between δ 6.9 and 7.3 (15 H) in the ^{1}H NMR indicate the presence of the PPh_3 ligand. Acidolysis of **2a** with gaseous HCl and the reaction of **2a** with MeI gave $HSC_2H_4OCH(CF_3)_2$ and $MeSC_2H_4OCH(CF_3)_2$ with concomitant formation of [AuCl(PPh_3)][15] and [AuI(PPh_3)][16] in quantitative yields, respectively. These facts support the formation of **2a**. Similar ring opening reactions of ethylene sulfide by other alkoxo- or aryloxo-gold(I) complexes [Au(OR)L] [R = $CH(CF_3)_2$, L = PCy_3 **1b**; R = Ph, L = PPh_3 **1c**, PCy_3 **1d** or PMe_3 **1e**] proceeded to form corresponding [2-(alkoxy- or aryloxy-)ethylthio]gold(I) complexes having tertiary phosphine ligands, [Au(SC_2H_4OR)L] [R = $CH(CF_3)_2$, L = PCy_3 **2b**; R = Ph, L = PPh_3 **2c**, PCy_3 **2d**; L = PMe_3 **2e**].

When unsymmetric thiiranes such as propylene sulfide, isobutylene sulfide and styrene sulfide were employed in this reaction the ring opening took place at the less hindered carbon with high regioselectivity. For example, the reaction of **1a** with propylene sulfide gave a mixture of two regioisomers of [Au{$SCHMeCH_2OCH(CF_3)_2$}(PPh_3)] **3a** and [Au{SCH_2-$CHMeOCH(CF_3)_2$}(PPh_3)] **3a′** in 90 : 10 ratio. These complexes could not be separated by recrystallisation because of their similar solubility. They were characterised by NMR, elemental analysis, and chemical reactions without isolation. The mixture of **3a** and **3a′** coincidentally shows only one singlet at δ 40.0 in ^{31}P-{^{1}H} NMR. The ^{1}H NMR spectrum of the major product **3a** shows a doublet at δ 1.80 (d, $J_{H\text{-}H}$ = 6.6 Hz, 3 H) and a doublet of quartets of doublets at δ 3.94 (dqd, $J_{H\text{-}H}$ = 9.9, 6.6, 4.2 Hz, 1 H) assignable to the methyl and the methine protons, respectively. Diastereotopic methylene protons appear as a triplet at δ 3.82 (t, $J_{H\text{-}H}$ = 9.9 Hz, 1 H) and a doublet of doublets at



Scheme 1

Table 1 Yield of (2-alkoxyethylsulfanyl)gold(I) complexes and their regioselectivity in the ring opening reaction of unsymmetric thiirane with alkoxo- or aryloxo-gold(I) complex

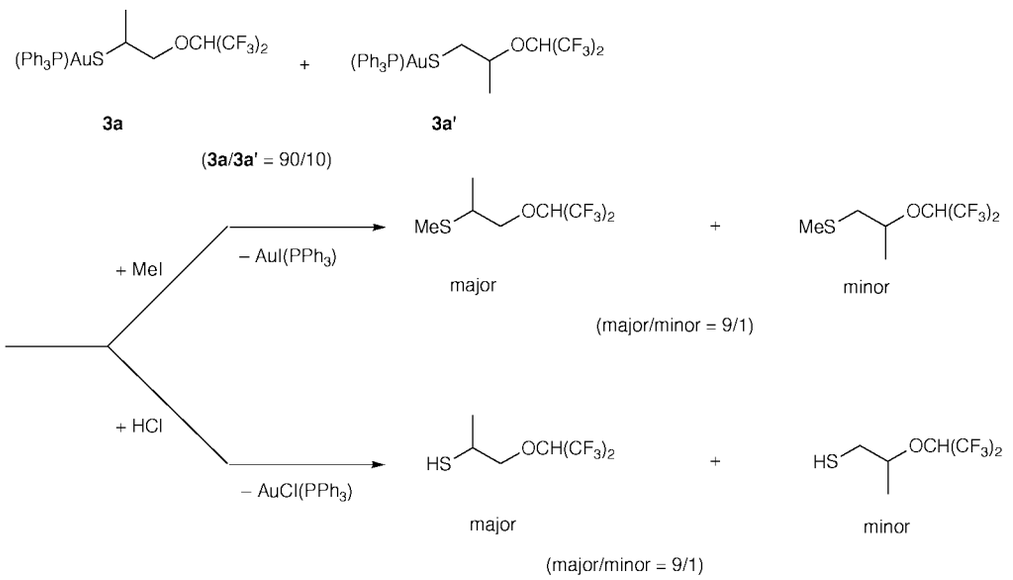
		(2-Alkoxyethylsulfanyl)gold(I) complex	
			Product ratio
Complex	Substrate	Yield (%)	
1a		47	90:10 (**3a**:**3a′**)
1b		88	82:18 (**3b**:**3b′**)
1c		65	67:33 (**3c**:**3c′**)
1d		73	87:13 (**3d**:**3d′**)
1e		100	68:32 (**3e**:**3e′**)
1a		88	98:2 (**4a**:**4a′**)
1b		94	96:4 (**4b**:**4b′**)
1c		74	98:2 (**4c**:**4c′**)
1d		52	97:3 (**4d**:**4d′**)
1e		95	86:14 (**4e**:**4e′**)
1a		83	77:23 (**5a**:**5a′**)
1b		65	97:3 (**5b**:**5b′**)
1c		34	65:35 (**5c**:**5c′**)
1d		57	73:27 (**5d**:**5d′**)

Conditions: thiirane = 1 equivalent per Au, r.t., solvent = thf, reaction time = 4 h.

δ 4.32 (dd, $J_{H\text{-}H}$ = 9.9, 4.2 Hz, 1 H). Similarly the ^{1}H NMR spectrum of the minor species **3a′** shows signals at δ 1.63 (d, $J_{H\text{-}H}$ = 6.0 Hz, 3 H) for the methyl group, δ 3.18 (dd, $J_{H\text{-}H}$ = 12.5, 9.3 Hz, 1 H) and 3.67 (dd, $J_{H\text{-}H}$ = 12.5, 3.9 Hz, 1 H) for diastereotopic methylene protons, although the resonance of the methine proton of the ethylthio fragment was obscured by overlapping with the signals of the major species.

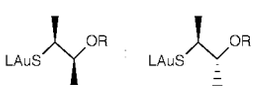
The regioselectivity of the reaction was further confirmed by the following chemical reactions with this mixture. Treatment with MeI in benzene afforded a mixture of the S-methylated products $MeSCHMeCH_2OCH(CF_3)_2$ and $MeSCH_2CHMeOCH(CF_3)_2$ in 90:10 ratio with concomitant formation of [AuI(PPh_3)] (99% yield), Scheme 2. These sulfides were characterised by ^{1}H NMR, GLC and GC-MS in which these regioisomers were clearly distinguished by their fragmentation patterns. Consistently, the reaction of the mixture of **3a** and **3a′** with HCl gas also gave $HSCHMeCH_2OCH(CF_3)_2$ and $HSCH_2CHMeOCH(CF_3)_2$ in 90:10 ratio with formation of [AuCl(PPh_3)], quantitatively. These data suggest that **3a** and **3a′** are [Au{$SCHMeCH_2OCH(CF_3)_2$}(PPh_3)] and [Au{$SCH_2CHMeOCH(CF_3)_2$}(PPh_3)], respectively. Similarly, regioselective ring opening reaction of propylene sulfide by a series of the alkoxo- and aryloxo-gold complexes **1b**–**1e** gave [Au{$SCHMeCH_2OCH(CF_3)_2$}(PCy_3)]/[Au{$SCH_2CHMeOCH(CF_3)_2$}(PCy_3)] (**3b**:**3b′** = 82:18), [Au($SCHMeCH_2OPh$)(PPh_3)]/[Au($SCH_2CHMeOPh$)(PPh_3)] (**3c**:**3c′** = 67:33), [Au($SCHMeCH_2OPh$)(PCy_3)]/[Au($SCH_2CHMeOPh$)(PCy_3)] (**3d**:**3d′** = 87:13) and [Au($SCHMeCH_2OPh$)(PMe_3)]/[Au($SCH_2CHMeOPh$)(PMe_3)] (**3e**:**3e′** = 68:32). In all cases, the major products were found to be the 1-methyl derivatives [Au($SCHMeCH_2OR$)L]. Ring opening reactions of other unsymmetrical thiiranes such as isobutylene sulfide and styrene sulfide with **1a**–**1e** similarly proceeded to yield [(2-alkoxy-1,1-dimethyl)ethylsulfanyl]gold(I) complexes **4a**–**4e** and [2-alkoxy-1-phenyl)ethylsulfanyl]gold(I) complexes **5a**–**5d** as major products, respectively. These results reveal that the alkoxo group dominantly attacks the less hindered carbon atom of thiiranes in these ring opening reactions. It is worthwhile to note that in the case of reactions of unsymmetric thiiranes with alcohols the alkoxo group is reported to attack the secondary or tertiary carbon atom of thiiranes by a proton-induced mechanism.[10]

In order to obtain further insights concerning the ring opening reaction, similar reactions with *cis*- and *trans*-2-butene sulfide were carried out. As a typical example, the reaction of complex **1c** with *cis*-2-butene sulfide exclusively gave *syn*-[Au($SCHMeCHMeOPh$)(PPh_3)] **6c** in 89% yield, indicating complete inversion at the carbon atom of *cis*-2-butene sulfide. The two methine protons of **6c** appeared at δ 4.37 (qd, J = 6.3, 3.3 Hz, 1 H) and 5.08 (qd, J = 6.3, 3.3 Hz, 1 H) in the ^{1}H NMR



Scheme 2

Table 2 Yield of *syn*- and *anti*-[2-(alkoxy- or -aryloxy-1,1-dimethyl)-ethylsulfanyl]gold(I) complexes and their stereoselectivity in the ring opening reaction of *cis*- or *trans*-2-butene sulfide with alkoxo- or aryloxo-gold(I) complexes

		[2-(Alkoxy- or -aryloxy-1,1-dimethyl)ethyl-sulfanyl]gold(I) complex	
			Product ratio
Complex	Substrate	Yield (%)	
1a		75	100:0 (**6a**:**6a′**)
1b		66	100:0 (**6b**:**6b′**)
1c		89	100:0 (**6c**:**6c′**)
1d		61	100:0 (**6d**:**6d′**)
1e		99	100:0 (**6e**:**6e′**)
1a		88	13:87 (**6a**:**6a′**)
1b		66	12:88 (**6b**:**6b′**)
1c		93	1:99 (**6c**:**6c′**)
1d		49	5:95 (**6d**:**6d′**)
1e		95	2:98 (**6e**:**6e′**)

[a] Conditions as in Table 1.

spectrum, showing a typical *syn* vicinal coupling constant.[17] On the other hand, reaction of **1c** with *trans*-2-butene sulfide yielded a diastereomeric mixture of *syn*- and *anti*-[Au(SCHMeCHMeOPh)(PPh_3)] **6c** and **6c′**, whose *syn*:*anti* ratio is 1:99. The two methine protons of the *anti* isomer **6c′** were observed at δ 4.10 (qd, J = 7.2, 6.6, 1 H) and 4.62 (dq, J = 6.6, 6.0 Hz, 1 H) in the ^{1}H NMR spectrum, where the vicinal coupling constant (J = 6.6 Hz) is clearly larger than that of **6c** (J = 3.3 Hz), suggesting the *anti* configuration. Other reactions of *cis*- and *trans*-2-butene sulfide with **1b**–**1e** also resulted in inversion at the carbon of 2-butene sulfide with high selectivity, suggesting an S_N2 type mechanism for these ring opening reactions (Table 2).

Without exception, reactions of complexes **1a**–**1e** with *cis*-2-butene sulfide exclusively gave *syn* forms **6a**–**6e**, while those with *trans*-2-butene sulfide gave diastereomeric mixtures though *anti* forms **6a′**–**6e′** were always dominant products. The observed high stereoselectivity in the reaction of *cis*-2-butene sulfide is most likely due to the smaller steric congestion at the carbon of *cis*-2-butene sulfide than that of *trans*-2-butene sulfide.

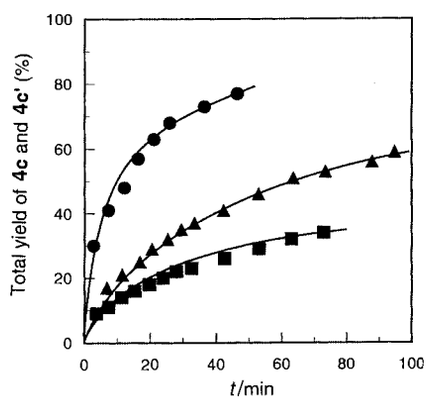


Fig. 1 Effect of the concentration of isobutylene sulfide on the reactions of [Au(OPh)(PPh_3)] **1c** with isobutylene sulfide. [**1c**] = 0.033 M, [isobutylene sulfide] = 0.066 (●), 0.033 (▲), 0.017 M (■), −10 °C, solvent = toluene-d_8.

Mechanism of the ring opening reaction

In order to shed some light on the reaction mechanism, time courses of the reaction of alkoxo- or aryloxo-gold(I) complexes with isobutylene sulfide were examined. The reactions were followed by ^{1}H NMR with a thermostatted probe at −10 °C using constant initial concentrations of gold complexes and thiiranes under N_2 in the presence of $CHPh_3$ as an internal standard.

The relative initial rates of the reaction of complex **1c** with different concentrations of isobutylene sulfide are shown in Fig. 1. When the concentration of isobutylene sulfide was increased from 0.017 to 0.033 and 0.066 M the initial rate for the formation of **4c** increased approximately twice and three times faster than that for 0.017 M, respectively. This fact suggests that the ring opening reaction is first order in the concentration of thiirane. On the other hand, when the concentration of **1c** was increased from 0.017 to 0.033 and 0.066 M in the presence of isobutylene sulfide (0.033 M) the initial rate increased approximately by factors of 4 and 9, respectively (Fig. 2).

This behaviour can be rationalised as second order rather than first order in the concentration of aryloxogold complex. Addition of KOPh (0.033 M) to a mixture of **1c** (0.033 M) and isobutylene sulfide (0.034 M) also increased the initial rate, although KOPh itself is inactive for the ring opening reaction of thiiranes under these conditions. The results suggest a

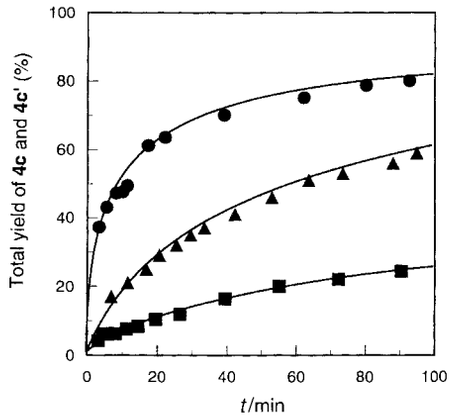


Fig. 2 Effect of the concentration of aryloxogold(I) complex on the reactions of [Au(OPh)(PPh_3)] **1c** with isobutylene sulfide. [**1c**] = 0.066 (●), 0.033 (▲), 0.017 M (■), [isobutylene sulfide] = 0.034 M, −10 °C, solvent = toluene-d_8.

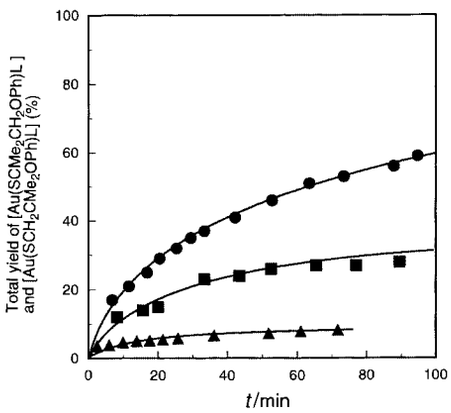


Fig. 3 Ligand effect for the reactions of [Au(OPh)L] with isobutylene sulfide. L = PPh_3 (●), PCy_3 (▲), PMe_3 (■). Other conditions as in Fig. 2.

bimolecular process between co-ordinated thiirane and the external alkoxide.

This reaction is strongly affected by the phosphine ligand in the gold(I) complex (Fig. 3). Triphenylphosphine complex **1c** is the fastest, followed by trimethylphosphine complex **1e** and tricyclohexylphosphine complex **1d**. The result may reflect the importance of the electrophilicity of the gold(I) fragment to co-ordinate the incoming thiirane. Addition of 1 equivalent of PPh_3 to the reaction mixture of **1c** decreased the reaction rate to approximately one third, suggesting the presence of a prerequisite process such as dissociation of PPh_3 or competitive co-ordination of PPh_3 and thiirane to the [Au(OR)(PPh_3)] complex (see below).

The reactions are significantly dependent on the solvent used as seen in Fig. 4. The reaction is faster in chloroform-d_1 (relative permittivity, $\varepsilon_r = 4.81$) than in toluene-d_8 ($\varepsilon_r = 2.38$), while tetrahydrofuran (thf)-d_8 ($\varepsilon_r = 7.20$) significantly retarded the reaction. It is worth noting that when tetrahydrothiophene was employed as the solvent **1c** remained unchanged.

From these kinetic results, a mechanism including co-ordination of thiirane to Au has been proposed as shown in Scheme 3. Suppression of the reaction by added PPh_3 suggests either dissociative path *a* or associative path *b* followed by the ring opening reaction (see below). However, the dissociative pathway (path *a*) is less likely because of the following reasons: (*i*) the observed gold complexes were only the starting compounds [Au(OR)L] **1**, and the product complex [Au(SCHMeCHMeOR)L] under catalytic conditions throughout the reaction according to ^1H and ^{31}P NMR. When 1 equivalent of PPh_3 was added to the reaction mixture at −10 °C, signals of **1c** (δ 27.8) and free PPh_3 (δ −4.5) were observed as one broad peak

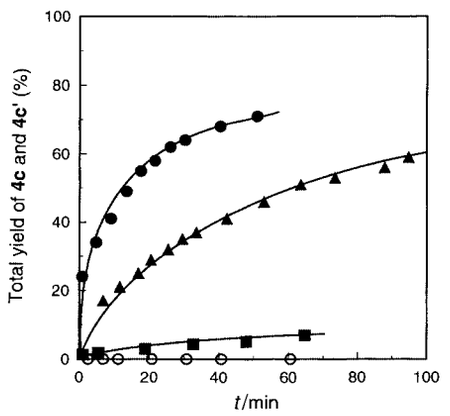
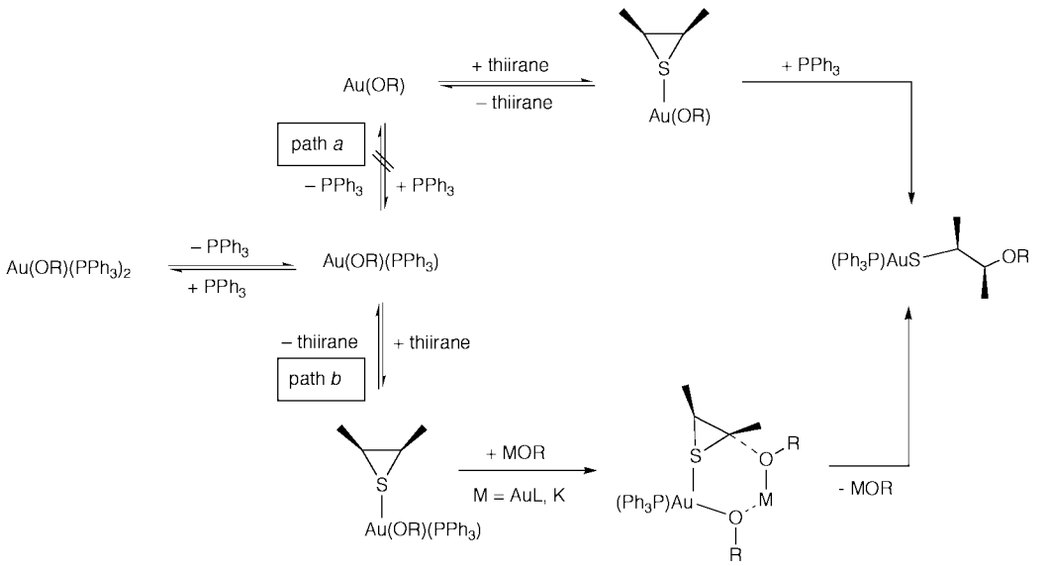


Fig. 4 Solvent effect for the reactions of [Au(OPh)(PPh_3)] **1c** with isobutylene sulfide. [**1c**] = 0.033 M, [isobutylene sulfide] = 0.034 M, −10 °C, solvent = chloroform-d_1 (●), toluene-d_8 (▲), thf-d_8 (■), tetrahydrothiophene (○).

at δ 19.1 (half width = 136 Hz) in the ^{31}P-{^1H} NMR. This fact indicates that the ligand exchange process, which is much faster than the ring opening reaction, is taking place. However, the observed chemical shift is far downfield in comparison with that expected from the simple fast exchange between **1a** and free PPh_3 (*ca.* δ 11.7). This suggests the associative formation of unreactive [Au(OR)L_2] species in the presence of free PPh_3. If the ^{31}P chemical shift of [Au(OR)L_2] is assumed to be similar to that of **1a**, approximately half of **1a** is considered to be converted into [Au(OR)L_2], consistent with the observed retardation effect of added PPh_3. On the other hand, a possible prior dissociation of PPh_3 giving reactive species [Au(OR)] is excluded, since addition of one equivalent PPh_3 should decrease such a minor dissociated species much more drastically under these conditions. (*ii*) As shown in Fig. 3, the reaction rate is significantly dependent on the phosphine ligand in gold(I) complex. Although PCy_3 ligand is considered to be more prone to dissociate than PMe_3 due to its steric bulkiness, the reaction rate of the PCy_3 complex is slower, being inconsistent with path *a.* This trend can be explained by prior association of **1** with thiirane, where steric congestion at Au is larger in **1d** than **1e** when thiirane co-ordinates. It is worth noting that KOPh never reacts with thiiranes under these conditions. Thus, thiirane is likely to co-ordinate to the alkoxogold(I) complex giving [Au(OR)(thiirane)L] as a first step. The electron donating phosphine ligand reduces the Lewis acidity of the gold(I) complex, discouraging the co-ordination of thiirane. Such initial co-ordination to the metal centre is also postulated for the ring opening reaction of thiiranes promoted by Ir–Zr and Ta complexes,[12a,b] and Adams and his co-workers[14] reported isolation of a thiirane complex of tungsten. Therefore prior co-ordination of thiiranes to the gold centre is considered to be indispensable for the reaction. This is likely due to the softness of the gold(I) fragment and the prior co-ordination results in enhancement of electrophilicity of thiiranes. Complete retardation in tetrahydrothiophene may be due to the strong co-ordination ability of this solvent, preventing the prior co-ordination of thiiranes to Au. Secondly, the external alkoxo moiety of the alkoxogold complex or KOPh attacks the less hindered carbon atom with inversion of configuration. This may explain the second order dependence on the alkoxogold complex concentration in the reaction. This would proceed *via* an S_N2 type mechanism because the stereochemistry at the carbon of thiirane involves inversion of configuration. However, ionic dissociation of these alkoxides is less likely, since no significant enhancement in polar solvent was observed. A possible intramolecular concerted reaction is also excluded for the ring opening reaction because this mechanism is inconsistent not only with the second order kinetics in the concentration of alkoxogold(I) complexes, but also with the



Scheme 3

stereochemistry at the carbon of thiirane. Thus, a bimolecular concerted mechanism (Scheme 3) is proposed for the ring opening reaction.

As a summary, selective ring opening reactions of thiiranes have been achieved by alkoxo- and aryloxo-gold complexes to give new 2-(alkoxy- or aryloxy-)ethylsulfanylgold(I) complexes under ambient conditions.

Experimental

All manipulations were performed under dry nitrogen using standard Schlenk and vacuum-line techniques unless otherwise noted. Benzene, toluene and hexane were dried over anhydrous calcium chloride, Et_2O and thf over calcium hydride and distilled from potassium–benzophenone or sodium wire prior to use. Dimethyl sulfoxide (dmso) and tetrahydrothiophene were dried over P_2O_5, and distilled under vacuum prior to use. Alkoxo- and aryloxo-gold(I) complexes **1a**–**1e** were prepared according to the procedure published in our previous papers.[3–6] Ethylene sulfide was purchased from Aldrich and used as received. Other sulfides such as propylene sulfide, isobutylene sulfide, styrene sulfide, and *cis*- and *trans*-2-butene sulfides were prepared from corresponding epoxides by using the literature method.[8] The ^{1}H and ^{31}P-{^{1}H} NMR spectra were recorded on a JEOL LA-300 (^{1}H, 300.4 MHz; ^{31}P, 121.55 MHz) spectrometer and chemical shifts are reported in ppm from tetramethylsilane and from external 85% H_3PO_4 for ^{1}H and ^{31}P-{^{1}H} NMR spectra, respectively. The IR spectra were recorded on a JASCO FT/IR-410 spectrometer. GLC analyses were performed with Shimadzu GC-8A or 14B gas liquid phase chromatographs using a glass packed PEG-20M or capillary TC-wax column with a flame ionisation detector. GC-MS spectra were recorded on a Shimadzu QP-2000 instrument at 70 eV. Elemental analyses were performed by a Perkin-Elmer 2400 series II CHNS analyser. Melting points were measured by a YAMATO MP-21 apparatus, and the values were uncorrected.

Reactions of alkoxo- and aryloxo-gold(I) complexes

With ethylene sulfide. As a typical example, the reaction of [Au{OCH(CF$_3$)$_2$}(PPh$_3$)] **1a** with ethylene sulfide giving [Au{SCH$_2$CH$_2$OCH(CF$_3$)$_2$}(PPh$_3$)] **2a** is described. Ethylene sulfide (0.0150 cm^3, 0.250 mmol) was added to a thf solution (5 cm^3) of complex **1a** (147.7 mg, 0.236 mmol) and the reaction mixture was stirred at room temperature for 4 h. Then all volatile matters were removed under reduced pressure and the resulting white powder was washed with hexane and then dried *in vacuo*. Recrystallisation of the residue from diethyl ether–hexane gave a white powder of [Au{SCH$_2$CH$_2$OCH(CF$_3$)$_2$}(PPh$_3$)] **2a** (93.4 mg, 0.15 mmol, 66%). ^{1}H NMR (C$_6$D$_6$) δ 3.42 (sep, $^3J_{H\text{-}F}$ = 6.6, 1 H, CH(CF$_3$)$_2$), 3.46 (t, $^3J_{H\text{-}H}$ = 7.9, 2 H, SCH$_2$C*H*$_2$O), 4.02 (t, $^3J_{H\text{-}H}$ = 7.9 Hz, 2 H, SC*H*$_2$CH$_2$O) and 6.9–7.3 (m, 15 H, PPh$_3$); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 36.8 (s); IR (KBr, cm^{-1}) 1480m, 1435m, 1374s, 1293s, 1227m, 1186s and 982m; mp (decomp.) 124–125 °C; Found: C, 40.55; H, 3.00; S, 4.36. Calc. for $C_{23}H_{20}AuF_6OPS$: C, 40.25; H, 2.94; S, 4.67%.

[Au{SCH$_2$CH$_2$OCH(CF$_3$)$_2$}(PCy$_3$)] **2b**. From complex **1b** (22.2 mg, 0.034 mmol) and ethylene sulfide (0.002 10 cm^3, 0.035 mmol). Yield 18.7 mg, 0.026 mmol, 77%. ^{1}H NMR (C$_6$D$_6$) δ 0.90–1.75 (m, 33 H, PC*y*$_3$), 3.52 (t, $^3J_{H\text{-}H}$ = 7.8, 2 H, SCH$_2$C*H*$_2$O), 3.59 (sep, $^3J_{H\text{-}F}$ = 6.0, 1 H, CH(CF$_3$)$_2$) and 4.13 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 2 H, SC*H*$_2$CH$_2$O); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 57.0 (s); mp (decomp.) 135–136 °C; Found: C, 39.68; H, 5.01; S, 4.51. Calc. for $C_{23}H_{28}AuF_6OPS$: C, 39.21; H, 5.44; S, 4.55%.

[Au(SCH$_2$CH$_2$OPh)(PPh$_3$)] **2c**. From complex **1c** (31.4 mg, 0.057 mmol) and ethylene sulfide (0.0064 cm^3, 0.065 mmol). Yield 25.4 mg, 0.041 mmol, 73%. ^{1}H NMR (C$_6$D$_6$) δ 3.79 (t, $^3J_{H\text{-}H}$ = 7.5, 2 H, SCH$_2$C*H*$_2$O), 4.47 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 2 H, SC*H*$_2$CH$_2$O) and 6.8–7.4 (m, 20 H, PPh$_3$ and OPh); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 35.7 (s); mp (decomp.) 159–160 °C; Found: C, 50.86; H, 4.06; S, 5.26. Calc. for $C_{26}H_{24}AuOPS$: C, 50.99; H, 3.95; S, 5.24%.

[Au(SCH$_2$CH$_2$OPh)(PCy$_3$)] **2d**. From complex **1d** (15.3 mg, 0.027 mmol) and ethylene sulfide (0.0016 cm^3, 0.027 mmol). Yield 10.0 mg, 0.016 mmol, 66%. ^{1}H NMR (C$_6$D$_6$) δ 1.0–1.8 (m, 33 H, PCy$_3$), 3.84 (t, $^3J_{H\text{-}H}$ = 8.1, 2 H, SCH$_2$C*H*$_2$O), 4.56 (t, $^3J_{H\text{-}H}$ = 8.1, 2 H, SC*H*$_2$CH$_2$O), 7.22 (dd, $^3J_{H\text{-}H}$ = 7.8, $^3J_{H\text{-}P}$ = 6.9, 2 H, *o*-H of OPh), 7.02 (t, $^3J_{H\text{-}H}$ = 7.8, 2 H, *m*-H of OPh) and 6.84 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1 H, *p*-H of OPh); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 54.5 (s); IR (KBr, cm^{-1}) 2924s, 2849s, 1587m, 1484m, 1446m, 1238m and 1004m; mp (decomp.) 162–163 °C; Found: C, 49.79; H, 6.84; S, 5.22. Calc. for $C_{26}H_{42}AuOPS$: C, 49.52; H, 6.71; S, 5.08%.

[Au(SCH$_2$CH$_2$OPh)(PMe$_3$)] **2e**. From complex **1e** (9.5 mg, 0.025 mmol) and ethylene sulfide (0.001 50 cm^3, 0.025 mmol). Yield 0.025 mmol, 99%. ^{1}H NMR (C$_6$D$_6$) δ 0.609 (d, $^2J_{H\text{-}P}$ = 10.2, 9 H, PMe$_3$), 3.74 (t, $^3J_{H\text{-}H}$ = 7.5, 2 H, SCH$_2$C*H*$_2$O), 4.47 (t, $^3J_{H\text{-}H}$ = 7.5, 2 H, SC*H*$_2$CH$_2$O), 7.1–7.4 (m, 4 H, *o*-, *m*-H of OPh) and 6.81 (t, 1 H, $^3J_{H\text{-}H}$ = 7.2 Hz, *p*-H of OPh). ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ −0.98 (s).

With propylene sulfide. From the reaction of complex **1a** (107.0 mg, 0.171 mmol) with propylene sulfide (0.0140 cm^3, 0.18 mmol) followed by similar work up to that described above, two regioisomers [Au{$SCHMeCH_2OCH(CF_3)_2$}(PPh_3)] **3a** and [Au{$SCH_2CHMeOCH(CF_3)_2$}(PPh_3)] **3a′** were obtained in 90 : 10 ratio, respectively. Yield 56.0 mg, 0.80 mmol, 47%. **3a**: ^{1}H NMR (C_6D_6) δ 1.80 (d, $^3J_{H\text{-}H}$ = 6.6, 3 H, SCH*Me*CH_2O), 3.42 (sep, $^3J_{H\text{-}F}$ = 6.0, 1 H, C*H*$(CF_3)_2$), 3.82 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 9.9, 1 H, SCHMeC*H*$_2$O), 3.94 (dqd, $^2J_{H\text{-}H}$ = 9.9, $^3J_{H\text{-}H}$ = 6.6, 4.2, 1 H, SC*H*MeCH_2O), 4.32 (dd, $^3J_{H\text{-}H}$ = 9.9, 4.2 Hz, 1 H, SCHMeC*H*$_2$O) and 6.8–7.3 (m, 15 H, PPh_3); ^{31}P-{^{1}H} NMR (C_6D_6) δ 40.0 (s). **3a′**: ^{1}H NMR (C_6D_6) δ 1.63 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, SCH_2CH*Me*O), 3.18 (dd, $^2J_{H\text{-}H}$ = 12.5, $^3J_{H\text{-}H}$ = 9.3, 1 H, SC*H*$_2$CHMeO) and 3.67 (dd, $^2J_{H\text{-}H}$ = 12.5, $^3J_{H\text{-}H}$ = 3.9 Hz, 1 H, SC*H*$_2$CHMeO); the two methine protons in the S{C*H*$(CH_3)CH_2OC$*H*$(CF_3)_2$} fragment and phenyl protons are obscured by overlapping with the signals of the major species **3a**; ^{31}P-{^{1}H} NMR (C_6D_6) δ 40.0 (s); IR (KBr, cm^{-1}) 1480m, 1460m, 1294s, 1232s, 1188s, 1101s and 980s; mp (decomp.) 189–190 °C; Found C, 40.95; H, 2.98; S, 4.79; Calc. for $C_{24}H_{22}AuF_6OPS$ C, 41.15; H, 3.17; S, 4.58%.

[Au{$SCHMeCH_2OCH(CF_3)_2$}(PCy_3)] **3b** and [Au{$SCH_2CHMeOCH(CF_3)_2$}(PCy_3)] **3b′**. From complex **1b** (29.2 mg, 0.045 mmol) and propylene sulfide (0.003 60 cm^3, 0.046 mmol). Yield 28.2 mg, 0.040 mmol, 88%. **3b** : **3b′** = 82 : 18. **3b**: ^{1}H NMR (C_6D_6) δ 0.8–1.7 (m, 33 H, PCy_3), 1.81 (d, $^3J_{H\text{-}H}$ = 6.3, 3 H, SCH*Me*CH_2O), 3.82 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 9.6, 1 H, SCHMeC*H*$_2$O), 4.01 (dqd, $^3J_{H\text{-}H}$ = 9.6, 6.3, 4.9, 1 H, SC*H*MeCH_2O) and 4.29 (dd, $^2J_{H\text{-}H}$ = 9.6, $^3J_{H\text{-}H}$ = 6.9 Hz, 1 H, SCHMeC*H*$_2$O); ^{31}P-{^{1}H} NMR (C_6D_6) δ 57.0 (s). **3b′**: ^{1}H NMR (C_6D_6) δ 1.89 (d, $^3J_{H\text{-}H}$ = 6.3, 3 H, SCH_2CH*Me*O), 3.84 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 9.5, 1 H, SC*H*$_2$CHMeO) and 4.31 (dd, $^2J_{H\text{-}H}$ = 9.5, $^3J_{H\text{-}H}$ = 4.2 Hz, 1 H, SC*H*$_2$CHMeO); ^{31}P-{^{1}H} NMR (C_6D_6) δ 57.0 (s); IR (KBr, cm^{-1}) 2929s, 2854s, 1448m, 1377m, 1286s, 1214s, 1191s, 1102s and 978s; mp (decomp.) 175–176 °C; Found C, 40.18; H, 5.85; S, 4.67; Calc. for $C_{24}H_{40}AuF_6OPS$ C, 40.12; H, 5.61; S, 4.46%.

[Au($SCHMeCH_2OPh$)(PPh_3)] **3c** and [Au($SCH_2CHMeOPh$)(PPh_3)] **3c′**. From complex **1c** (42.1 mg, 0.077 mmol) and propylene sulfide (0.0060 cm^3, 0.077 mmol). Yield, 30.8 mg, 0.050 mmol, 65%. **3c** : **3c′** = 67 : 33. **3c**: ^{1}H NMR (C_6D_6) δ 1.93 (d, $^3J_{H\text{-}H}$ = 6.6, 3 H, SCH*Me*CH_2O), 4.22 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 9.4, 1 H, SCHMeC*H*$_2$O), 4.31 (dqd, $^2J_{H\text{-}H}$ = 9.4, $^3J_{H\text{-}H}$ = 6.6, 3.9, 1 H, SC*H*MeCH_2O), 4.74 (dd, $^3J_{H\text{-}H}$ = 3.9 Hz, 2 H, SCHMeC*H*$_2$O) and 6.7–7.3 (m, 20 H, OPh, PPh_3); ^{31}P-{^{1}H} NMR (C_6D_6) δ 40.0 (s). **3c′**: ^{1}H NMR (C_6D_6) δ 1.84 (d, $^3J_{H\text{-}H}$ = 5.7, 3 H, SCH_2CH*Me*O), 3.41 (dd, $^2J_{H\text{-}H}$ = 12.7, $^3J_{H\text{-}H}$ = 8.4, 1 H, SC*H*$_2$CHMeO) and 3.89 (dd, $^2J_{H\text{-}H}$ = 12.7, $^3J_{H\text{-}H}$ = 3.6 Hz, 1 H, SC*H*$_2$CHMeO); ^{31}P-{^{1}H} NMR (C_6D_6) δ 40.0 (s); mp (decomp.) 153–154 °C; Found C, 52.09; H, 4.12; S, 5.09; Calc. for $C_{27}H_{26}AuOPS$ C, 51.76; H, 4.18; S, 5.12%.

[Au($SCHMeCH_2OPh$)(PCy_3)] **3d** and [Au($SCH_2CHMeOPh$)(PCy_3)] **3d′**. From complex **1d** (20.9 mg, 0.037 mmol) and propylene sulfide (0.0030 cm^3, 0.038 mmol). Yield 18.3 mg, 0.027 mmol, 73%. **3d** : **3d′** = 87 : 13. **3d**: ^{1}H NMR (C_6D_6) δ 0.9–1.7 (m, 33 H, PCy_3), 1.98 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, SCH*Me*CH_2O), 4.22 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 9.2, 1 H, SCHMeC*H*$_2$O), 4.31 (dqd, $^2J_{H\text{-}H}$ = 9.2, $^3J_{H\text{-}H}$ = 6.0, 3.8, 1 H, SC*H*MeCH_2O), 4.79 (dd, $^3J_{H\text{-}H}$ = 9.2, 3.8, 1 H, SC*H*MeCH_2O), 6.81 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1 H, *p*-H of OPh) and 7.0–7.2 (m, 4 H, *o*-, *m*-H of OPh); ^{31}P-{^{1}H} NMR (C_6D_6) δ 56.8 (s). **3d′**: ^{1}H NMR (C_6D_6) δ 1.84 (d, $^3J_{H\text{-}H}$ = 5.7, 3 H, SCH_2CH*Me*O), 3.41 (dd, $^2J_{H\text{-}H}$ = 12.3, $^3J_{H\text{-}H}$ = 3.3, 1 H, SC*H*$_2$CHMeO) and 4.02 (dd, $^2J_{H\text{-}H}$ = 12.3, $^3J_{H\text{-}H}$ = 9.3 Hz, 1 H, SC*H*$_2$CHMeO); ^{31}P-{^{1}H} NMR (C_6D_6) δ 56.8 (s); mp (decomp.) 112–113 °C; Found C, 50.86; H, 6.78; S, 5.03; Calc. for $C_{27}H_{44}AuOPS$ C, 50.31; H, 6.88; S, 4.97%.

[Au($SCHMeCH_2OPh$)(PMe_3)] **3e** and [Au($SCH_2CHMeOPh$)(PMe_3)] **3e′**. From complex **1e** (10.0 mg, 0.026 mmol) and propylene sulfide (0.0021 cm^3, 0.027 mmol). Yield 0.026 mmol, 100%. **3e** : **3e′** = 68 : 32. **3e**: ^{1}H NMR (C_6D_6) δ 0.60 (d, $^2J_{H\text{-}P}$ = 10.5, 9 H, PMe_3), 1.90 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, SCH*Me*CH_2O), 4.15 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 9.3, 1 H, SCHMeC*H*$_2$O), 4.22 (dqd, $^2J_{H\text{-}H}$ = 9.3, $^3J_{H\text{-}H}$ = 6.0, 3.6, 1 H, SC*H*MeCH_2O), 4.66 (dd, $^3J_{H\text{-}H}$ = 9.3, 3.6, 1 H, SC*H*MeCH_2O), 4.22 (dqd, $^2J_{H\text{-}H}$ = 9.3, $^3J_{H\text{-}H}$ = 6.0, 3.8 Hz, 1 H, SCHMeC*H*$_2$O) and 7.0–7.4 (m, 5 H, OPh); ^{31}P-{^{1}H} NMR (C_6D_6) δ −2.12 (s). **3e′**: ^{1}H NMR (C_6D_6) δ 0.60 (d, $^2J_{H\text{-}P}$ = 10.5, 9 H, P*Me*$_3$), 1.73 (d, $^3J_{H\text{-}H}$ = 6.3, 3 H, SCH_2CH*Me*O), 3.35 (dd, $^2J_{H\text{-}H}$ = 12.5, $^3J_{H\text{-}H}$ = 8.4, 1 H, SC*H*$_2$CHMeO), 3.75 (dqd, $^2J_{H\text{-}H}$ = 12.5, $^3J_{H\text{-}H}$ = 8.4, 3.9, 1 H, SCH_2C*H*MeO) and 3.83 (dd, $^2J_{H\text{-}H}$ = 12.6, $^3J_{H\text{-}H}$ = 3.9 Hz, 1 H, SC*H*$_2$CHMeO); ^{31}P-{^{1}H} NMR (C_6D_6) δ −2.12 (s).

With isobutylene sulfide. From the reaction of complex **1a** (101.4 mg, 0.161 mmol) and isobutylene sulfide (0.0140 cm^3, 0.18 mmol) followed by similar work-up to that described above, [Au{$SCMe_2CH_2OCH(CF_3)_2$}(PPh_3)] **4a** and [Au{$SCH_2CMe_2OCH(CF_3)_2$}(PPh_3)] **4a′** were obtained in 98 : 2 ratio, respectively. Yield 101.0 mg, 0.141 mmol, 87.8%. **4a**: ^{1}H NMR (C_6D_6) δ 1.92 (s, 6 H, SC*Me*$_2$$CH_2$O), 3.42 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, OC*H*$(CF_3)_2$), 4.12 (s, 2 H, $SCMe_2$C*H*$_2$O) and 6.8–7.3 (m, 15 H, PPh_3); ^{31}P-{^{1}H} NMR (C_6D_6) δ 39.9 (s). **4a′**: ^{1}H NMR (C_6D_6) δ 1.64 (s, 6 H, SCH_2C*Me*$_2$O), 3.84 (s, 2 H, SC*H*$_2$$CMe_2$O) and 4.38 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, OC*H*$(CF_3)_2$); ^{31}P-{^{1}H} NMR (C_6D_6) δ 39.9 (s); IR (KBr, cm^{-1}) 1480m, 1435m, 1297s, 1230s, 1188m, 1109s and 998m; mp (decomp.) 163–164 °C; Found C, 42.25; H, 3.40; S, 4.45; Calc. for $C_{25}H_{24}AuF_6OPS$ C, 42.03; H, 3.39; S, 4.49%.

[Au{$SCMe_2CH_2OCH(CF_3)_2$}(PCy_3)] **4b** and [Au{$SCH_2CMe_2OCH(CF_3)_2$}(PCy_3)] **4b′**. Reaction of complex **1b** (23.1 mg, 0.035 mmol) with isobutylene sulfide (0.0035 cm^3, 0.036 mmol). Yield 24.9 mg, 0.034 mmol, 94%. **4b** : **4b′** = 96 : 4. **4b**: ^{1}H NMR (C_6D_6) δ 0.9–1.7 (m, 33 H, PCy_3), 1.94 (s, 6 H, SC*Me*$_2$$CH_2$O), 3.58 (sep, $^3J_{H\text{-}F}$ = 6.0, OC$H(CF_3)_2$) and 4.13 (s, 2 H, $SCMe_2$C*H*$_2$O); ^{31}P-{^{1}H} NMR (C_6D_6) δ 57.0 (s). **4b′**: ^{1}H NMR (C_6D_6) δ 3.76 (s, 2 H, SC*H*$_2$$CMe_2$O) and 4.62 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, OC*H*$(CF_3)_2$); ^{31}P-{^{1}H} NMR (C_6D_6) δ 57.0 (s); mp (decomp.) 147–148 °C; Found C, 40.88; H, 5.74; S, 4.68; Calc. for $C_{25}H_{42}AuF_6OPS$ C, 40.99; H, 5.78; S, 4.38%.

[Au($SCMe_2CH_2OPh$)(PPh_3)] **4c** and [Au(SCH_2CMe_2OPh)(PPh_3)] **4c′**. From complex **1c** (36.2 mg, 0.065 mmol) and isobutylene sulfide (0.006 4 cm^3, 0.065 mmol). Yield 31.4 mg, 0.048 mmol, 74%. **4c** : **4c′** = 98 : 2. **4c**: ^{1}H NMR (C_6D_6) δ 2.00 (s, 6 H, SC*Me*$_2$$CH_2$O), 4.48 (s, 2 H, $SCMe_2$C*H*$_2$O) and 6.7–7.3 (m, 20 H, OPh, PPh_3); ^{31}P-{^{1}H} NMR (C_6D_6) δ 40.0 (s). **4c′**: ^{1}H NMR (C_6D_6) δ 1.64 (s, 6 H, SCH_2C*Me*$_2$O) and 3.79 (s, 2 H, SC*H*$_2$$CMe_2$O); ^{31}P-{^{1}H} NMR ($C_6D_6$) δ 40.0 (s); IR (KBr, cm^{-1}) 1597m, 1580m, 1491m, 1435m, 1240m and 985m; mp (decomp.) 139–140 °C; Found C, 52.44; H, 4.46; S, 5.39; Calc. for $C_{28}H_{28}AuOPS$ C, 52.50; H, 4.41; S, 5.01%.

[Au($SCMe_2CH_2OPh$)(PCy_3)] **4d** and [Au(SCH_2CMe_2OPh)(PCy_3)] **4d′**. From complex **1d** (20.3 mg, 0.035 mmol) and isobutylene sulfide (0.0035 cm^3, 0.035 mmol). Yield 12.1 mg, 0.018 mmol, 52%. **4d** : **4d′** = 97 : 3. **4d**: ^{1}H NMR (C_6D_6) δ 0.9–1.7 (m, 33 H, PCy_3), 2.13 (s, 6 H, SC*Me*$_2$$CH_2$O), 4.52 (s, 2 H, $SCMe_2$C*H*$_2$O) and 6.8–7.2 (m, 5 H, OPh); ^{31}P-{^{1}H} NMR (C_6D_6) δ 56.8 (s). **4d′**: ^{1}H NMR (C_6D_6) δ 3.67 (s, SC*H*$_2$$CMe_2$O); ^{31}P-{^{1}H} NMR ($C_6D_6$) δ 56.8 (s); mp (decomp.) 142–143 °C; Found C, 50.98; H, 7.23; S, 4.66; Calc. for $C_{28}H_{46}AuOPS$ C, 51.06; H, 7.04; S, 4.87%.

[Au($SCMe_2CH_2OPh$)(PMe_3)] **4e** and [Au(SCH_2CMe_2OPh)(PMe_3)] **4e′**. From complex **1e** (11.1 mg, 0.020 mmol) and isobutylene sulfide (0.0020 cm^3, 0.020 mmol). Yield 0.019 mmol, 95%. **4e** : **4e′** = 86 : 14. **4e**: ^{1}H NMR (C_6D_6) δ 0.74 (d, $^2J_{H\text{-}P}$ = 10.2 Hz, 9 H, PMe_3), 1.92 (s, 6 H, SC*Me*$_2$$CH_2$O), 4.33 (s, 2 H, CMe_2C*H*$_2$O) and 6.8–7.3 (m, 5 H, OPh); ^{31}P-{^{1}H} NMR (C_6D_6) δ −10.3 (s). **4e′**: ^{1}H NMR (C_6D_6) δ 0.74 (d, $^2J_{H\text{-}P}$ = 10.2 Hz, 9 H, PMe_3), 1.63 (s, 6 H, SCH_2C*Me*$_2$OPh) and 3.57 (s, 2 H, CMe_2C*H*$_2$O); ^{31}P-{^{1}H} NMR (C_6D_6) δ −10.3 (s).

With styrene sulfide. From the reaction of complex **1a** (70.3 mg, 0.101 mmol) with styrene sulfide (15.5 mg, 0.11

mmol) followed by similar work-up to that described above, [Au{SCHPhCH$_2$OCH(CF$_3$)$_2$}(PPh$_3$)] **5a** and [Au{SCH$_2$CHPhOCH(CF$_3$)$_2$}(PPh$_3$)] **5a′** were obtained in 77:23 ratio, respectively. Yield 69.4 mg, 0.091 mmol, 83%. **5a**: ^{1}H NMR (C$_6$D$_6$) δ 3.74 (dd, $^3J_{H\text{-}H}$ = 12.9, $^3J_{H\text{-}H}$ = 9.0, 1 H, SCHPhCH_2O), 4.02 (dd, $^2J_{H\text{-}H}$ = 12.9, $^3J_{H\text{-}H}$ = 4.8, 1 H, SCHPhCH_2O), 4.16 (sep, $^3J_{H\text{-}F}$ = 6.3, 1 H, OCH(CF$_3$)$_2$), 5.02 (dd, $^2J_{H\text{-}H}$ = 9.0, $^3J_{H\text{-}H}$ = 4.8 Hz, 1 H, SC*H*PhCH$_2$O) and 6.9–7.8 (m, 20 H, SCH*Ph*CH$_2$O, PPh$_3$); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 37.29 (s). **5a′**: ^{1}H NMR (C$_6$D$_6$) δ 4.58 (dd, $^2J_{H\text{-}H}$ = 9.0, $^3J_{H\text{-}H}$ = 4.5, 1 H, SCH$_2$-C*H*PhO) and 4.45 (sep, $^3J_{H\text{-}F}$ = 5.4 Hz, 1 H, OC*H*(CF$_3$)$_2$); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 37.29 (s). mp (decomp.) 127–128 °C; Found C, 46.06; H, 3.04; S, 4.30; Calc. for C$_{29}$H$_{24}$AuF$_6$OPS C, 45.68; H, 3.17; S, 4.21%.

[Au{SCHPhCH$_2$OCH(CF$_3$)$_2$}(PCy$_3$)] **5b** and [Au{SCH$_2$CHPhOCH(CF$_3$)$_2$}(PCy$_3$)] **5b′**. From complex **1b** (69.0 mg, 0.11 mmol) and styrene sulfide (16.3 mg, 0.12 mmol). Yield 54.6 mg, 0.70 mmol, 65%. **5b**:**5b′** = 97:3. **5b**: ^{1}H NMR (C$_6$D$_6$) δ 0.7–1.7 (m, 33 H, PCy$_3$), 3.72 (dd, $^3J_{H\text{-}H}$ = 12.8, $^3J_{H\text{-}H}$ = 7.9, 1 H, SCHPhCH_2O), 4.03 (dd, $^2J_{H\text{-}H}$ = 12.8, $^3J_{H\text{-}H}$ = 5.1, 1 H, SCHPhCH_2O), 4.16 (sep, $^3J_{H\text{-}F}$ = 6.3, 1 H, OCH(CF$_3$)$_2$), 5.08 (dd, $^2J_{H\text{-}H}$ = 7.9, $^3J_{H\text{-}H}$ = 5.1 Hz, 1 H, SC*H*PhCH$_2$O) and 7.0–7.5 (m, 5 H, CH*Ph*); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 54.24 (s). **5b′**: ^{1}H NMR (C$_6$D$_6$) δ 4.35 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 10.2, 1 H, SCH_2CHPhO) and 4.97 (dd, $^2J_{H\text{-}H}$ = 10.2, $^3J_{H\text{-}H}$ = 4.5 Hz, 1 H, SCH_2CHPhO); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 54.24 (s); mp (decomp.) 156–157 °C; Found C, 44.99; H, 5.74; S, 4.25; Calc. for C$_{29}$H$_{42}$AuF$_6$OPS C, 44.62; H, 5.42; S, 4.11%.

[Au(SCHPhCH$_2$OPh)(PPh$_3$)] **5c** and [Au(SCH$_2$CHPhOPh)(PPh$_3$)] **5c′**. From complex **1c** (68.9 mg, 0.12 mmol) and styrene sulfide (18.3 mg, 0.13 mmol). Yield 28.1 mg, 0.041 mmol, 34%. **5c**:**5c′** = 65:35. **5c**: ^{1}H NMR (C$_6$D$_6$) δ 3.82 (dd, $^2J_{H\text{-}H}$ = 12.9, $^3J_{H\text{-}H}$ = 6.9, 1 H, SCHPhCH_2O), 4.60 (t, $^3J_{H\text{-}H}$ = 6.9, 1 H, SC*H*PhCH$_2$O), 5.08 (dd, $^2J_{H\text{-}H}$ = 12.9, $^3J_{H\text{-}H}$ = 6.9 Hz, 1 H, SCHPhCH_2O) and 6.9–7.8 (m, 25 H, SCH*Ph*CH$_2$O, OPh, PPh$_3$); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 38.3 (s). **5c′**: ^{1}H NMR (C$_6$D$_6$) δ 3.55 (dd, $^2J_{H\text{-}H}$ = 12.3, $^3J_{H\text{-}H}$ = 9.3, 1 H, SCH_2CHPhO) and 4.12 (dd, $^2J_{H\text{-}H}$ = 12.3, $^3J_{H\text{-}H}$ = 7.2 Hz, 1 H, SCH_2CHPhO); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 38.3 (s); mp (decomp.) 166–167 °C.

[Au(SCHPhCH$_2$OPh)(PCy$_3$)] **5d** and [Au(SCH$_2$CHPhOPh)(PCy$_3$)] **5d′**. From complex **1d** (20.5 mg, 0.036 mmol) and styrene sulfide (5.04 mg, 0.037 mmol). Yield 14.5 mg, 0.020 mmol, 57%. **5d**:**5d′** = 73:27. **5d**: ^{1}H NMR (C$_6$D$_6$) δ 0.7–1.7 (m, 33 H, PCy$_3$), 3.72 (dd, $^3J_{H\text{-}H}$ = 12.8, $^3J_{H\text{-}H}$ = 7.9, 1 H, SCHPhCH_2O), 4.03 (dd, $^2J_{H\text{-}H}$ = 12.8, $^3J_{H\text{-}H}$ = 5.1, 1 H, SCHPhCH_2O), 5.08 (dd, $^2J_{H\text{-}H}$ = 7.9, $^3J_{H\text{-}H}$ = 5.1 Hz, 1 H, SC*H*PhCH$_2$O) and 6.9–7.4 (m, 10 H, SCH*Ph*CH$_2$O, OPh); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 53.8 (s) **5d′**: ^{1}H NMR (C$_6$D$_6$) δ 4.35 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 10.2, 1 H, SCH_2CHPhO) and 4.97 (dd, $^2J_{H\text{-}H}$ = 10.2, $^3J_{H\text{-}H}$ = 4.5 Hz, 1 H, SCH_2CHPhO); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 53.8 (s); mp (decomp.) 134–135 °C.

With *cis*-2-butene sulfide. From the reaction of complex **1a** (103.2 mg, 0.164 mmol) and *cis*-2-butene sulfide (0.0160 cm^3, 0.180 mmol) followed by work-up as above, *syn*-[Au{SCHMeCHMeOCH(CF$_3$)$_2$}(PPh$_3$)] **6a** was exclusively obtained. Yield 90.4 mg, 0.13 mmol, 75%. ^{1}H NMR (C$_6$D$_6$) δ 1.62 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, CH*Me*), 1.74 (d, $^3J_{H\text{-}H}$ = 6.9, 3 H, CH*Me*), 3.72 (sep, $^3J_{H\text{-}F}$ = 6.0, 1 H, OCH(CF$_3$)$_2$), 4.13 (qd, $^3J_{H\text{-}H}$ = 6.9, 3.6, 1 H, C*H*Me), 4.32 (qd, $^3J_{H\text{-}H}$ = 6.0, 3.6 Hz, 1 H, C*H*Me), 6.8–6.9 (m, 9 H, *m*-, *p*-H of OPh) and 7.2–7.3 (m, 6 H, *o*-H of OPh); ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 39.5 (s); IR (KBr, cm^{-1}) 1481m, 1436m, 1217s, 1191s, 1131m, 1102s and 968m; mp (decomp.) 141–142 °C; Found: C, 41.89; H, 3.38; S, 4.45. Calc. for C$_{25}$H$_{24}$AuF$_6$OPS: C, 42.03; H, 3.39; S, 4.49%.

syn-[Au{SCHMeCHMeOCH(CF$_3$)$_2$}(PCy$_3$)] **6b**. From complex **1b** (53.2 mg, 0.082 mmol) and *cis*-2-butene sulfide (0.0100 cm^3, 0.085 mmol). Yield 40.2 mg, 0.054 mmol, 66%. ^{1}H NMR (C$_6$D$_6$) δ 0.8–1.7 (m, 39 H, CH*Me*, PCy$_3$), 3.90 (sep, $^3J_{H\text{-}F}$ = 6.0, 1 H, C*H*(CF$_3$)$_2$), 4.12 (qd, $^3J_{H\text{-}H}$ = 6.8, 3.9, 1 H, C*H*Me) and 4.31 (qd, $^3J_{H\text{-}H}$ = 8.0, 3.9 Hz, 1 H, C*H*Me). ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 57.1 (s); mp (decomp.) 144–145 °C; Found: C, 41.32; H, 5.54; S, 4.32. Calc. for C$_{25}$H$_{42}$AuF$_6$OPS: C, 40.99; H, 5.78; S, 4.38%.

syn-[Au(SCHMeCHMeOPh)(PPh$_3$)] **6c**. From complex **1c** (49.3 mg, 0.089 mmol) and *cis*-2-butene sulfide (0.0086 cm^3, 0.091 mmol). Yield 51.0 mg, 0.080 mmol, 89%. ^{1}H NMR (C$_6$D$_6$) δ 1.70 (d, $^3J_{H\text{-}H}$ = 6.3, 6 H, CH*Me*), 4.37 (qd, $^3J_{H\text{-}H}$ = 6.3, 3.3, 1 H, SC*H*Me), 5.08 (qd, $^3J_{H\text{-}H}$ = 6.3, 3.3 Hz, 1 H, C*H*Me) and 6.7–7.5 (m, 20 H, OPh, PPh$_3$). ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 36.0 (s); mp (decomp.) 171–172 °C; Found: C, 52.38; H, 4.58; S, 5.10. Calc. for C$_{28}$H$_{28}$AuOPS: C, 52.50; H, 4.41; S, 5.01%.

syn-[Au(SCHMeCHMeOPh)(PCy$_3$)] **6d**. From complex **1d** (20.3 mg, 0.035 mmol) and *cis*-2-butene sulfide (0.0033 cm^3, 0.035 mmol). Yield 14.1 mg, 0.021 mmol, 61%. ^{1}H NMR (C$_6$D$_6$) δ 0.9–1.7 (m, 33 H, PCy$_3$), 1.72 (d, $^3J_{H\text{-}H}$ = 6.9, 3 H, CH*Me*), 1.83 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, CH*Me*), 4.43 (qd, $^3J_{H\text{-}H}$ = 6.0, 3.3, 1 H, C*H*Me), 5.13 (qd, $^3J_{H\text{-}H}$ = 6.9, 3.3, 1 H, C*H*Me), 6.81 (t, $^3J_{H\text{-}H}$ = 6.8, 1 H, *p*-H of OPh), 7.02 (t, $^3J_{H\text{-}H}$ = 6.8, 2 H, *m*-H of OPh) and 7.19 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 2 H, *o*-H of OPh). ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 56.9 (s); mp (decomp.) 129–130 °C; Found: C, 50.89; H, 7.13; S, 4.92. Calc. for C$_{28}$H$_{46}$AuOPS: C, 51.06; H, 7.04; S, 4.87%.

syn-[Au(SCHMeCHMeOPh)(PMe$_3$)] **6e**. From complex **1e** (9.6 mg, 0.025 mmol) and *cis*-2-butene sulfide (0.0026 cm^3, 0.027 mmol). Yield 0.025 mmol, 99%. ^{1}H NMR (C$_6$D$_6$) δ 0.57 (d, $^2J_{H\text{-}P}$ = 10.5, 9 H, P*Me*$_3$), 1.74 (d, $^3J_{H\text{-}H}$ = 3.6, 6 H, CH*Me*), 4.27 (qd, $^3J_{H\text{-}H}$ = 6.9, 3.0, 1 H, C*H*Me), 5.03 (qd, $^3J_{H\text{-}H}$ = 6.9, 3.6 Hz, 1 H, C*H*Me) and 6.8–7.2 (m, 5 H, OPh). ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ −0.41s.

With *trans*-2-butene sulfide. From the reaction of complex **1a** (92.3 mg, 0.147 mmol) and *trans*-2-butene sulfide (0.0160 cm^3, 0.150 mmol) followed by similar work-up to that described above, a mixture of *syn*-[Au{SCHMeCHMeOCH(CF$_3$)$_2$}(PPh$_3$)] **6a** and *anti*-[Au{SCHMeCHMeOCH(CF$_3$)$_2$}(PPh$_3$)] **6a′** was obtained in 13:87 ratio, respectively. Yield 93.2 mg, 0.13 mmol, 88%. **6a′**: ^{1}H NMR (C$_6$D$_6$) δ 1.62 (d, $^3J_{H\text{-}H}$ = 5.4, 3 H, SCHMeCH*Me*O), 2.01 (d, $^3J_{H\text{-}H}$ = 5.7, 3 H, SCH*Me*CHMeO), 3.84 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, 1 H, OCH(CF$_3$)$_2$), 3.72 (m, 2 H, C*H*Me), 6.8–6.9 (m, 9 H, *m*-, *p*-H of OPh) and 7.2–7.3 (m, 6 H, *o*-H of Ph). ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 39.8 (s). Following data were measured for the mixture of **6a** and **6a′**. IR (KBr, cm^{-1}): 1463m, 1438m, 1286s, 1235m, 1210s, 1101s and 967m; mp (decomp.) 138–139 °C; Found: C, 42.16; H, 3.25; S, 4.68%.

syn-[Au{SCHMeCHMeOCH(CF$_3$)$_2$}(PCy$_3$)] **6b** and *anti*-[Au{SCHMeCHMeOCH(CF$_3$)$_2$}(PCy$_3$)] **6b′**. From complex **1b** (50.0 mg, 0.078 mmol) and *trans*-2-butene sulfide (0.0100 cm^3, 0.080 mmol). Yield 48.3 mg, 0.065 mmol, 66%. **6b**:**6b′** = 12:88. **6b′**: ^{1}H NMR (C$_6$D$_6$) δ 0.8–1.7 (m, 39 H, CH*Me*, PCy$_3$), 3.78 (qui, $^3J_{H\text{-}H}$ = 6.3, 1 H, SC*H*MeCHMeO), 3.94 (qui, $^3J_{H\text{-}H}$ = 6.0, 1 H, SCHMeC*H*MeO) and 4.13 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, 1 H, CH(CF$_3$)$_2$). ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 57.0 (s); mp (decomp.) 153–154 °C; Found: C, 40.78; H, 5.67; S, 4.21. Calc. for C$_{25}$H$_{42}$AuF$_6$OPS: C, 40.99; H, 5.78; S, 4.38%.

syn-[Au(SCHMeCHMeOPh)(PPh$_3$)] **6c** and *anti*-[Au(SCHMeCHMeOPh)(PPh$_3$)] **6c′**. From complex **1c** (50.2 mg, 0.090 mmol) and *trans*-2-butene sulfide (0.0090 cm^3, 0.091 mmol). Yield 54.2 mg, 0.084 mmol, 93%. **6c**:**6c′** = 1:99. **6c′**: ^{1}H NMR (C$_6$D$_6$) δ 1.82 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, SCHMeCH*Me*O), 1.94 (d, $^3J_{H\text{-}H}$ = 7.2, 3 H, SCHMeCH*Me*O), 4.10 (qd, $^3J_{H\text{-}H}$ = 7.2, 6.6 Hz, 1 H, SC*H*MeCHMeO), 4.62 (dq, $^3J_{H\text{-}H}$ = 6.6, 6.0 Hz, 1 H, SCHMeC*H*MeO) and 6.7–7.3 (m, 20 H, OPh, PPh$_3$). ^{31}P-{^{1}H} NMR (C$_6$D$_6$) δ 40.0 (s); mp (decomp.) 172–173 °C; Found: C, 52.36; H, 4.25; S, 5.22. Calc. for C$_{28}$H$_{28}$AuOPS: C, 52.50; H, 4.41; S, 5.01%.

syn-[Au(SCHMeCHMeOPh)(PCy$_3$)] **6d** and *anti*-[Au(SCHMeCHMeOPh)(PCy$_3$)] **6d′**. From complex **1d** (21.4 mg, 0.036 mmol) and *trans*-2-butene sulfide (0.0036 cm^3, 0.036 mmol). Yield 12.4 mg, 0.018 mmol, 49%. **6d**:**6d′** = 5:95. **6d′**:

^{1}H NMR (C_6D_6) δ 0.9–1.7 (m, 33 H, PCy_3), 1.92 (d, $^3J_{H\text{-}H}$ = 5.7, 3 H, SCHMeCH*Me*O), 2.02 (d, $^3J_{H\text{-}H}$ = 6.3, 3 H, SCH*Me*CHMeO), 4.08 (qd, $^3J_{H\text{-}H}$ = 8.0, 6.3, 1 H, SC*H*MeCHMeO), 4.57 (qd, $^3J_{H\text{-}H}$ = 8.0, 5.7 Hz, 1 H, SCHMeC*H*MeO), 6.8 (m, 1 H, *p*-H of OPh), 7.0 (m, 2 H, *m*-H of OPh) and 7.21 (t, $^3J_{H\text{-}H}$ = 6.3, 2 H, *o*-H of OPh); ^{31}P-{^{1}H} NMR (C_6D_6) δ 56.1 (s); mp (decomp.) 120–121 °C; Found: C, 52.34; H, 4.28; S, 5.01. Calc. for $C_{28}H_{28}AuOPS$: C, 52.50; H, 4.41; S, 5.01%.

syn-[Au(SCHMeCHMeOPh)(PMe_3)] **6e′** and *anti*-[Au(SCHMeCHMeOPh)(PMe_3)] **6e′**. From complex **1e** (9.7 mg, 0.026 mmol) and *trans*-2-butene sulfide (0.0026 cm^3, 0.026 mmol). Yield 0.025 mmol, 95%. **6e**:**6e′** = 2:98. **6e′**: ^{1}H NMR (C_6D_6): δ 0.56 (d, $^2J_{H\text{-}P}$ = 10.2, 9 H, PMe_3), 1.75 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, SCHMeCH*Me*O), 1.92 (d, $^3J_{H\text{-}H}$ = 6.6, 3 H, SCH*Me*CHMeO), 4.03 (qui, $^3J_{H\text{-}H}$ = 6.6, 1 H, SC*H*MeCHMeO), 4.60 (qui, $^3J_{H\text{-}H}$ = 6.0 Hz, 1 H, SCHMeC*H*MeO) and 6.8–7.4 (m, 5 H, OPh); ^{31}P-{^{1}H} NMR (C_6D_6) δ −2.03 (s).

Reaction of compounds 2–6 with MeI

As a typical example, the reaction of a mixture of complexes **3a** and **3a′** with MeI is described. Methyl iodide (0.0140 cm^3, 0.180 mmol) was added into the mixture of **3a** and **3a′** (107.2 mg, 0.171 mmol) in thf (2 cm^3). After stirring for 2 h at room temperature two peaks appeared in 90:10 integration ratio by GLC, which were also characterised by GC-MS. The integration ratio **3a**:**3a′** was estimated as equal as to the molar ratio, since they are regioisomers. GC-MS (EI: 70 eV): $MeSCHMeCH_2OCH(CF_3)_2$ (major species), *m*/*z* = 256 [M^+, $MeSCHMeCH_2OCH(CF_3)_2$], 241 [$(CF_3)_2CHOCH_2CHMeS^+$], 209 [$(CF_3)_2CHOCH_2CHMe^+$], 181 [$(CF_3)_2CHOCH_2^+$] and 75 ($MeSCH_2^+$); $MeSCH_2CHMeOCH(CF_3)_2$ (minor species), *m*/*z* = 256 [M^+, $MeSCH_2CHMeOCH(CF_3)_2$], 241 [$(CF_3)_2CHOCH_2CHMeS^+$], 209 [$(CF_3)_2CHOCH_2CHMe^+$] and 195 [$(CF_3)_2CHOCH_2^+$]. This reaction was also carried out in a NMR tube. Methyl iodide (0.0011 cm^3, 0.018 mmol) was added to a mixture of **3a** and **3a′** (11.9 mg, 0.0170 mmol, **3a**:**3a′** = 90:10) and $CHPh_3$ as an internal standard (10.3 mg, 0.042 mmol) in benzene-d_6 (0.6 cm^3), and ^{1}H and ^{31}P-{^{1}H} NMR spectra were measured at room temperature. The NMR spectra showed formation of two sulfides $MeSCHMeCH_2OCH(CF_3)_2$ and $MeSCH_2CHMeOCH(CF_3)_2$ in 90:10 ratio, and known [AuI(PPh_3)].[16] $MeSCHMeCH_2OCH(CF_3)_2$: ^{1}H NMR (C_6D_6) δ 1.70 (s, 3 H, SMe), 1.77 (d, $^3J_{H\text{-}H}$ = 6.3, 3 H, SCH*Me*CH_2O), 3.41 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, 1 H, C*H*$(CF_3)_2$), 3.77 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 10.2, 1 H, SCHMeC*H*$_2$O), 3.92 (dqd, $^2J_{H\text{-}H}$ = 10.2, $^3J_{H\text{-}H}$ = 6.3, 4.5, 1 H, SC*H*MeCH$_2$O) and 4.27 (dd, $^3J_{H\text{-}H}$ = 10.2, 4.5 Hz, 2 H, SCHMeC*H*$_2$O). $MeSCH_2CHMeOCH(CF_3)_2$: ^{1}H NMR (C_6D_6) δ 1.05 (d, $^3J_{H\text{-}H}$ = 6.9, 3 H, SCH$_2$CH*Me*O), 1.57 (s, 3 H, SMe), 3.25 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 9.5, 1 H, SC*H*$_2$CHMeO) and 3.34 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, 1 H, OC$H(CF_3)_2$).

2a. $MeSCH_2CH_2OCH(CF_3)_2$. Yield 96%. GC-MS (EI: 70 eV): *m*/*z* = 242 [M^+, $MeSCH_2CH_2OCH(CF_3)_2$], 195 [$(CF_3)_2CHOCH_2CH_2^+$], 181 [$(CF_3)_2CHOCH_2^+$] and 61 ($MeSCH_2^+$). ^{1}H NMR (C_6D_6): δ 1.65 (s, 3 H, SMe), 3.24 (sep, $^3J_{H\text{-}F}$ = 6.6, 1 H, C$H(CF_3)_2$), 2.17 (t, $^3J_{H\text{-}H}$ = 8.4, 2 H, SCH$_2$C*H*$_2$O) and 3.32 (t, $^3J_{H\text{-}H}$ = 8.4 Hz, 2 H, SC*H*$_2$CH$_2$O).

2b. $MeSCH_2CH_2OCH(CF_3)_2$. Yield 98%.

2c. $MeSCH_2CH_2OPh$. Yield 96%. GC-MS (EI: 70 eV): *m*/*z* = 168 (M^+, $MeSCH_2CH_2OPh$), 121 ($PhOCH_2CH_2^+$) and 61 ($MeSCH_2^+$). ^{1}H NMR (C_6D_6) δ 1.76 (s, 3 H, SMe), 2.49 (t, $^3J_{H\text{-}H}$ = 7.2, 2 H, SCH$_2$C*H*$_2$O), 3.75 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 2 H, SC*H*$_2$CH$_2$O) and 7.0–7.4 (m, 5 H, OPh).

2d. $MeSCH_2CH_2OPh$. Yield 97%.

3b/3b′. $MeSCHMeCH_2OCH(CF_3)_2$ and $MeSCH_2CHMeOCH(CF_3)_2$. Yield 96%, ratio = 82:18 (GLC), 80:20 (NMR).

3c/3c′. $MeSCHMeCH_2OPh$ and $MeSCH_2CHMeOPh$. Yield 98%, ratio = 69:31 (GLC). GC-MS (EI: 70 eV): $MeSCHMeCH_2OPh$ (major species), *m*/*z* = 182 (M^+, $MeSCHMeCH_2OPh$), 135 ($PhOCH_2CHMe^+$) and 107 ($PhOCH_2^+$); $MeSCH_2CHMeOPh$ (minor species), *m*/*z* = 182 (M^+, $MeSCH_2CHMeOPh$), 121 ($PhOCHMe^+$) and 61 ($MeSCH_2^+$).

3d/3d′. $MeSCHMeCH_2OPh$ and $MeSCH_2CHMeOPh$. Yield 97%, ratio = 84:16 (GLC).

4a/4a′. $MeSCMe_2CH_2OCH(CF_3)_2$ and $MeSCH_2CMe_2OCH(CF_3)_2$. Yield 98%, ratio = 98:2 (GLC), 99:1 (NMR). GC-MS (EI: 70 eV): $MeSCMe_2CH_2OCH(CF_3)_2$ (major species), *m*/*z* = 270 [M^+, $MeSCMe_2CH_2OCH(CF_3)_2$], 255 [$(CF_3)_2CHOCH_2CMe_2S^+$], 223 [$(CF_3)_2CHOCH_2CMe_2^+$], 181 [$(CF_3)_2CHOCH_2^+$] and 89 ($MeSCMe_2^+$); $MeSCH_2CMe_2OCH(CF_3)_2$ (minor species), *m*/*z* = 270 [M^+, $MeSCH_2CMe_2OCH(CF_3)_2$], 255 [$(CF_3)_2CHOCMe_2CH_2S^+$], 209 [$(CF_3)_2CHOCMe_2^+$] and 61 ($MeSCH_2^+$). $MeSCMe_2CH_2OCH(CF_3)_2$: ^{1}H NMR (C_6D_6) δ 1.10 (s, 6 H, SC*Me*$_2$CH$_2$O), 1.79 (s, 3 H, SMe), 3.26 (s, 2 H, SCMe$_2$C*H*$_2$O) and 3.56 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, OC$H(CF_3)_2$). $MeSCH_2CMe_2OCH(CF_3)_2$: ^{1}H NMR (C_6D_6) δ 1.67 (s, 6 H, SCH$_2$C*Me*$_2$O), 1.96 (s, 3 H, SMe) and 3.20 (sep, $^3J_{H\text{-}F}$ = 6.0, OC$H(CF_3)_2$).

4b/4b′. $MeSCMe_2CH_2OCH(CF_3)_2$ and $MeSCH_2CMe_2OCH(CF_3)_2$. Yield 97%, ratio = 96:4 (GLC), 90:10 (NMR).

4c/4c′. $MeSCMe_2CH_2OPh$ and $MeSCH_2CMe_2OPh$. Yield 89%, ratio = 98:2 (GLC), 96:4 (NMR). GC-MS (EI: 70 eV): $MeSCMe_2CH_2OPh$ (major species), *m*/*z* = 196 (M^+, $MeSCMe_2CH_2OPh$), 149 ($PhOCH_2CMe_2^+$) and 107 ($PhOCH_2^+$); $MeSCH_2CMe_2OPh$ (minor species), *m*/*z* = 196 (M^+, $MeSCH_2CMe_2OPh$), 135 ($PhOCMe_2^+$) and 61 ($MeSCH_2^+$). $MeSCMe_2CH_2OPh$: ^{1}H NMR (C_6D_6) δ 1.10 (s, 6 H, SC*Me*$_2$CH$_2$O), 1.79 (s, 3 H, SMe) and 3.26 (s, 2 H, SCMe$_2$C*H*$_2$O). $MeSCH_2CMe_2OPh$: ^{1}H NMR (C_6D_6) δ 1.22 (s, 6 H, SCH$_2$C*Me*$_2$O), 1.73 (s, 3 H, SMe) and 3.74 (s, 2 H, SC*H*$_2$CMe$_2$O).

4d/4d′. $MeSCMe_2CH_2OPh$ and $MeSCH_2CMe_2OPh$. Yield 89%, ratio = 97:3 (GLC), 95:5 (NMR).

5a/5a′. $MeSCHPhCH_2OCH(CF_3)_2$ and $MeSCH_2CHPhOCH(CF_3)_2$. Yield 87%, ratio = 75:25 (GLC). GC-MS (EI: 70 eV): $MeSCHPhCH_2OCH(CF_3)_2$ (major species), *m*/*z* = 318 [M^+, $MeSCHPhCH_2OCH(CF_3)_2$], 271 [$(CF_3)_2CHOCH_2CHPh^+$] and 181 [$(CF_3)_2CHOCH_2^+$]; $MeSCH_2CHPhOCH(CF_3)_2$ (minor species), *m*/*z* = 318 [M^+, $MeSCH_2CHPhOCH(CF_3)_2$], 303 [$(CF_3)_2CHOCHPhCH_2S^+$] and 257 [$(CF_3)_2CHOCHPh^+$].

5b/5b′. $MeSCHPhCH_2OCH(CF_3)_2$ and $MeSCH_2CHPhOCH(CF_3)_2$. Yield 89%, ratio = 95:5 (GLC).

5c/5c′. $MeSCHPhCH_2OPh$ and $MeSCH_2CHPhOPh$. Yield 95%, ratio = 70:30 (GLC). GC-MS (EI: 70 eV): $MeSCHPhCH_2OPh$ (major species), *m*/*z* = 244 (M^+, $MeSCHPhCH_2OPh$), 197 ($PhOCH_2CHPh^+$) and 107 ($PhOCH_2^+$); $MeSCH_2CHPhOPh$ (minor species), *m*/*z* = 244 (M^+, $MeSCHPhCH_2OPh$), 224 ($PhOCHPhCH_2S^+$) and 183 ($PhOCHPh^+$).

5d/5d′. $MeSCHPhCH_2OPh$ and $MeSCH_2CHPhOCPh$. Yield 77%, ratio = 70:30 (GLC).

6a. *syn*-$MeSCHMeCHMeOCH(CF_3)_2$. Yield 99%. GC-MS (EI: 70 eV): *m*/*z* = 270 [M^+, $MeSCHMeCHMeOCH(CF_3)_2$], 223 [$(CF_3)_2CHOCHMeCHMe^+$] and 195 [$(CF_3)_2CHOCHMe^+$]. ^{1}H NMR (C_6D_6) δ 0.96 (d, $^3J_{H\text{-}H}$ = 6.3, 3 H, CH*Me*), 1.06 (d, $^3J_{H\text{-}H}$ = 7.2, 3 H, CH*Me*), 1.70 (s, 3 H, SMe), 2.53 (qd, $^3J_{H\text{-}H}$ = 7.2, 3.9, 1 H, C*H*Me), 3.38 (sep, $^3J_{H\text{-}F}$ = 6.0, 1 H, OC$H(CF_3)_2$) and 3.46 (qd, $^3J_{H\text{-}H}$ = 6.3, 3.9 Hz, 1 H, C*H*Me).

6b. *syn*-MeSCHMeCHMeOCH$(CF_3)_2$. Yield 98%.

6a/6a′. *anti*-MeSCHMeCHMeOCH$(CF_3)_2$. Yield 95%. GC-MS (EI: 70 eV): m/z = 270 [M^+, MeSCHMeCHMeOCH$(CF_3)_2$], 223 [$(CF_3)_2$CHOCHMeCHMe$^+$] and 195 [$(CF_3)_2$CHOCHMe$^+$]. ^{1}H NMR (C_6D_6) δ 1.41 (s, 3 H, SMe), 1.56 (d, $^3J_{H\text{-}H}$ = 6.9, 3 H, SCHMeCH*Me*O), 1.90 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, SCH*Me*CHMeO), 3.76 (m, 2 H, C*H*Me) and 3.86 (sep, $^3J_{H\text{-}F}$ = 6.0, 1 H, OCH$(CF_3)_2$). The *syn* isomer was not detected.

6b/6b′. *anti*-MeSCHMeCHMeOCH$(CF_3)_2$. Yield 98%.

Protonolysis of compounds 2–6 with HCl

As a typical example, the reaction of a mixture of complexes **3a** and **3a′** with HCl is described. Hydrogen chloride gas (0.733 ml, 0.030 mmol) was introduced into a mixture of **3a** and **3a′** (10.2 mg, 0.015 mmol) in thf (2 cm^3). After stirring for 2 h at room temperature, two peaks were observed in 90 : 10 integration ratio by GLC, which were also characterised by GC-MS. GC-MS (EI: 70 eV): HSCHMeCH$_2$OCH$(CF_3)_2$ (major species), m/z = 242 [M^+, HSCHMeCH$_2$OCH$(CF_3)_2$], 209 [$(CF_3)_2$CHOCH$_2$CHMe$^+$], 181 [$(CF_3)_2$CHOCH$_2^+$] and 61 (MeSCH$_2^+$); HSCH$_2$CHMeOCH$(CF_3)_2$ (minor species), m/z = 242 [M^+, HSCH$_2$CHMeOCH$(CF_3)_2$], 209 [$(CF_3)_2$CHOCHMeCH$_2^+$] and 181 [$(CF_3)_2$CHOCHMe$^+$]. This reaction was also carried out in a NMR tube: HCl (0.486 ml, 0.020 mmol) was added to the mixture of **3a** and **3a′** (10.2 mg, 0.015 mmol) and $(Me_3Si)_2O$ as an internal standard (0.0010 cm^3, 0.0047 mmol) in benzene-d_6 (0.6 cm^3). The ^{1}H NMR and ^{31}P-{^{1}H} spectra were immediately measured at room temperature. They showed formation of two sulfides HSCHMeCH$_2$OCH$(CF_3)_2$ and HSCH$_2$CHMeOCH$(CF_3)_2$ in 90 : 10 ratio, and known [AuCl(PPh$_3$)].[15] HSCHMeCH$_2$OCH$(CF_3)_2$: ^{1}H NMR (C_6D_6) δ 0.93 (d, $^3J_{H\text{-}H}$ = 6.9, 3 H, CH*Me*), 1.29 (d, $^3J_{H\text{-}H}$ = 6.9, 1 H, SH), 2.52 (sep, $^3J_{H\text{-}F}$ = 6.9, 1 H, CH$(CF_3)_2$), 3.03 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 8.1, 1 H, SCHMeC*H*$_2$O) and 3.23 (m, 2 H, SC*H*MeCH$_2$O, SCHMeC*H*$_2$O). HSCH$_2$CHMeOCH$(CF_3)_2$: ^{1}H NMR (C_6D_6) δ 0.80 (d, $^3J_{H\text{-}H}$ = 6.3, 3 H, SCH$_2$CHMeO), 1.12 (d, $^3J_{H\text{-}H}$ = 6.3, 1 H, SH), 2.12 (sep, $^3J_{H\text{-}F}$ = 6.0, 1 H, OCH$(CF_3)_2$) and 3.39 (t, $^2J_{H\text{-}H}$ = $^3J_{H\text{-}H}$ = 8.3 Hz, 1 H, SC*H*$_2$CHMeO).

2a. HSCH$_2$CH$_2$OCH$(CF_3)_2$. Yield 98%. GC-MS (EI: 70 eV): m/z = 196 [M^+, HSCH$_2$CH$_2$OCH$(CF_3)_2$], 163 [$(CF_3)_2$CHOCH$_2$CH$_2^+$] and 149 [$(CF_3)_2$CHOCH$_2^+$]. ^{1}H NMR (C_6D_6) δ 1.10 (t, $^3J_{H\text{-}H}$ = 8.5, 1 H, SH), 2.00 (q, $^3J_{H\text{-}H}$ = 8.5, 1 H, SCH$_2$C*H*$_2$O), 3.11 (t, $^3J_{H\text{-}H}$ = 8.5, 1 H, SC*H*$_2$CH$_2$O) and 3.17 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, 1 H, OCH$(CF_3)_2$).

2b. HSCH$_2$CH$_2$OCH$(CF_3)_2$. Yield 89%.

2c. HSCH$_2$CH$_2$OPh. Yield 96%. GC-MS (EI: 70 eV): m/z = 154 (M^+, HSCH$_2$CH$_2$OPh), 121 (PhOCH$_2$CH$_2^+$) and 107 (PhOCH$_2^+$). ^{1}H NMR (C_6D_6) δ 1.31 (t, $^3J_{H\text{-}H}$ = 8.1, 1 H, SH), 2.33 (q, $^3J_{H\text{-}H}$ = 8.1, 1 H, SC*H*$_2$CH$_2$), 3.53 (t, $^3J_{H\text{-}H}$ = 8.5, 1 H, SCH$_2$C*H*$_2$O), 6.8 (m, 3 H, *m*-, *p*-H of OPh) and 7.09 (d, $^3J_{H\text{-}H}$ = 6.8, 2 H, *o*-H of OPh).

2d. HSCH$_2$CH$_2$OPh. Yield 98%.

3a/3a′. HSCHMeCH$_2$OCH$(CF_3)_2$ and HSCH$_2$CHMeOCH$(CF_3)_2$. Yield 89%, ratio = 91 : 9 (GLC).

3c/3c′. HSCHMeCH$_2$OPh and HSCH$_2$CHMeOPh. Yield 94%. GC-MS (EI: 70 eV): HSCHMeCH$_2$OPh (major species), m/z = 168 (M^+, HSCHMeCH$_2$OPh), 135 (PhOCH$_2$CHMe$^+$) and 107 (PhOCH$_2^+$); HSCH$_2$CHMeOPh (minor species), m/z = 168 (M^+, HSCH$_2$CHMeOPh), 135 (PhOCHMeCH$_2^+$) and 121 (PhOCHMe$^+$).

3d/3d′. HSCHMeCH$_2$OPh and HSCH$_2$CHMeOPh. Yield 91%, ratio = 85 : 15 (GLC).

4a/4a′. HSCMe$_2$CH$_2$OCH$(CF_3)_2$ and HSCH$_2$CMe$_2$OCH$(CF_3)_2$. Yield 100%, ratio = 99 : 1 (GLC), 99 : 1 (NMR). GC-MS (EI: 70 eV): HSCMe$_2$CH$_2$OCH$(CF_3)_2$ (major species), m/z = 256 [M^+, HSCMe$_2$CH$_2$OCH$(CF_3)_2$], 223 [$(CF_3)_2$CHOCH$_2$CMe$_2^+$], 209 [$(CF_3)_2$CHOCH$_2^+$], 181 [$(CF_3)_2$CHOCH$_2^+$] and 89 (MeSCMe$_2^+$); HSCH$_2$CMe$_2$OCH$(CF_3)_2$ (minor species), m/z = 256 [M^+, HSCH$_2$CMe$_2$OCH$(CF_3)_2$], 223 [$(CF_3)_2$CHOCMe$_2$CH$_2^+$], 209 [$(CF_3)_2$CHOCMe$_2^+$] and 47 (HSCH$_2^+$). HSCMe$_2$CH$_2$OCH$(CF_3)_2$: ^{1}H NMR (C_6D_6) δ 1.07 (s, 6 H, SC*Me*$_2$CH$_2$O), 1.61 (s, 1 H, SH), 3.12 (s, 2 H, SCMe$_2$C*H*$_2$O) and 3.31 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, OCH$(CF_3)_2$). HSCH$_2$CMe$_2$OCH$(CF_3)_2$: ^{1}H NMR (C_6D_6) δ 0.77 (s, 6 H, SCH$_2$C*Me*$_2$O), 1.22 (s, 1 H, SH), 3.07 (d, $^3J_{H\text{-}H}$ = 6.8, 2 H, SC*H*$_2$CMe$_2$O).

4b/4b′. HSCMe$_2$CH$_2$OCH$(CF_3)_2$ and HSCH$_2$CMe$_2$OCH$(CF_3)_2$. Yield 95%, ratio = 96 : 4 (GLC), 98 : 2 (NMR).

4c/4c′. HSCMe$_2$CH$_2$OPh and HSCH$_2$CMe$_2$OPh. Yield 98%, ratio = 98 : 2 (GLC), 99 : 1 (NMR). GC-MS (EI: 70 eV): HSCMe$_2$CH$_2$OPh (major species), m/z = 182 (M^+, HSCMe$_2$CH$_2$OPh), 149 (PhOCH$_2$CMe$_2^+$) and 107 (PhOCH$_2^+$); HSCH$_2$CMe$_2$OPh (minor species), m/z = 182 (M^+, HSCH$_2$CMe$_2$OPh) and 135 (PhOCMe$_2^+$). HSCMe$_2$CH$_2$OPh: ^{1}H NMR (C_6D_6) δ 1.26 (s, 6 H, SC*Me*$_2$CH$_2$O), 1.90 (s, 3 H, S*H*), 3.54 (s, 2 H, SCMe$_2$CH$_2$O) and 7.03 (m, 5 H, OPh). HSCH$_2$CMe$_2$OPh: ^{1}H NMR (C_6D_6) δ 1.05 (s, 6 H, SCH$_2$CMe$_2$O) and 3.46 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, HSC*H*$_2$).

4d/4d′. HSCMe$_2$CH$_2$OPh and HSCH$_2$CMe$_2$OPh. Yield 89%, ratio = 97 : 3 (GLC), 95 : 5 (NMR).

6a. *syn*-HSCHMeCHMeOCH$(CF_3)_2$. Yield 99%. GC-MS (EI: 70 eV): m/z = 256 [M^+, HSCHMeCHMeOCH$(CF_3)_2$], 223 [$(CF_3)_2$CHOCHMeCHMe$^+$] and 195 [$(CF_3)_2$CHOCHMe$^+$].

6b. *syn*-MeSCHMeCHMeOCH$(CF_3)_2$. Yield 98%.

6a/6a′. *anti*-HSCHMeCHMeOCH$(CF_3)_2$. Yield 95%. GC-MS (EI: 70 eV): m/z = 256 [M^+, HSCHMeCHMeOCH$(CF_3)_2$], 223 [$(CF_3)_2$CHOCHMeCHMe$^+$] and 195 [$(CF_3)_2$CHOCHMe$^+$]. ^{1}H NMR (C_6D_6) δ 0.85 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, SCHMeCH*Me*O), 0.93 (d, $^3J_{H\text{-}H}$ = 12.6, 3 H, SCH*Me*CHMeO), 1.36 (d, $^3J_{H\text{-}H}$ = 6.0, 3 H, SH), 2.56 (sex, $^3J_{H\text{-}H}$ = 6.0, 1 H, SC*H*MeCHMeO), 3.11 (qui, $^3J_{H\text{-}H}$ = 6.0, 1 H, SCHMeC*H*MeO) and 3.46 (sep, $^3J_{H\text{-}F}$ = 6.0 Hz, 1 H, OCH$(CF_3)_2$). The *syn* isomer was not detected.

6b/6b′. *anti*-MeSCHMeCHMeOCH$(CF_3)_2$. Yield 98%. The *syn* isomer was not detected.

Time course of the ring opening reaction of thiiranes by alkoxogold(I) complexes

The phenoxogold(I) complex (0.020 mmol) and CHPh$_3$ (0.020 mmol) as an internal standard were placed in a 5 mm diameter NMR tube with a silicon rubber septum under nitrogen and freshly distilled toluene-d_8 (0.600 cm^3) was introduced by a hypodermic syringe. The NMR tube was placed in a thermostatted NMR probe at −10 ± 1 °C and a spectrum was measured. Immediately after ejection of the NMR tube a settled amount of isobutylene sulfide was injected by a microsyringe through a rubber septum to start the reaction and then the NMR tube was re-inserted into the thermostatted probe. Product yields were estimated periodically by comparing the peak areas of signals due to the product and the methine peak of CHPh$_3$ (δ 5.43) in the ^{1}H NMR spectra. The reactions finally

proceeded to 80–100% yields in most cases. The reactions in other solvents were carried out in a similar way.

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