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Au-Catalyzed Reaction of Propargylic Sulfides and Dithioacetals

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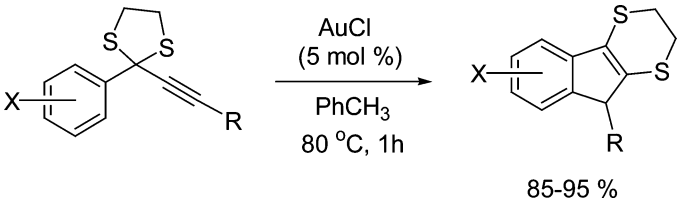
Received September 9, 2006



Propargylic sulfides and dithioacetals are found to undergo similar transformations as propargylic carboxylates when catalyzed by AuCl or $AuCl_3$, affording indene derivatives through pentannulation of aromatic rings. The reaction presumably involves Au carbene as the reactive intermediate.

Introduction

The chemistry of transition-metal-complex-activated alkynes has witnessed increasing development in recent years.[1] Among the various catalytic systems, Au(I) and Pt(II) complexes have attracted particular attention due to their high affinity to the π system of the alkyne substrates. A number of novel transformations have emerged based on the Au(I)- or Pt(II)-catalyzed reactions of alkynes.[2] One of the general processes that is involved in those transformations is the transition-metal-catalyzed reaction of propargyl esters that generates a metal carbene intermediate, as shown by eq 1.[1e,3] The activation of the triple bond by a transition metal triggers an intramolecular nucleophilic attack by the ester carbonyl oxygen, generating a cyclic five-centered ionic species. Subsequent 1,2-acyl group migration leads to the formation of a metal carbene.

Given the high affinity of gold to alkynes as well as the high reactivity of metal-activated alkynes toward nucleophiles, we have envisioned that other nucleophiles, such as a thio group or a halogen group, may also trigger a similar reaction through a three-centered ionic intermediate, which is generated by intramolecular 1,3-nucleophilic attack (eqs 2 and 3). Although sulfur-containing functional groups are known to have a strong coordination ability toward transition metals, recent reports demonstrate that the reaction of allenyl compounds bearing sulfur groups can also be catalyzed with transition-metal complexes. Gevorgyan and co-workers have reported 1,2-thio migration in Cu-catalyzed reactions of allenyl sulfides.[4] A recent

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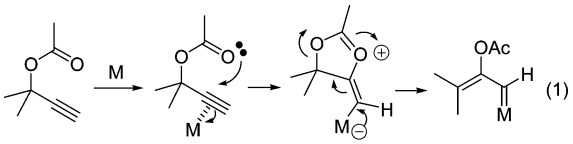
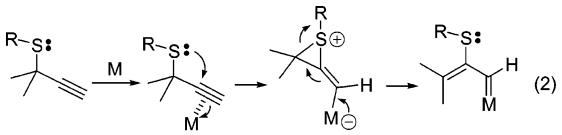
(2) For the selected, most recent developments, see: (a) Harrak, Y.; Blaszykowski, C.; Bernard, M.; Cariou, K.; Mainetti, E.; Mouriès, V.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *J. Am. Chem. Soc.* **2004**, *126*, 8656. (b) Luzung, M. R.; Markham, J. P.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 10858. (c) Fürstner, A.; Hannen, P. *Chem. Commun.* **2004**, 2546. (d) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 11806. (e) Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556. (f) Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 15978. (g) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402. (h) Gorin, D. J.; Davies, N. R.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 11260. (i) Kusama, H.; Yamabe, H.; Onizawa, Y.; Hoshino, T.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 468. (j) Antoniotti, S.; Genin, E.; Michelet, V.; Genêt, J.-P. *J. Am. Chem. Soc.* **2005**, *127*, 9976. (k) Fürstner, A.; Davies, P. W.; Gress, T. *J. Am. Chem. Soc.* **2005**, *127*, 8244. (l) Gagosz, F. *Org. Lett.* **2005**, *7*, 4129. (m) Markham, J. P.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 9708. (n) Suhre, M. H.; Reif, M.; Kirsch, S. F. *Org. Lett.* **2005**, *7*, 3925. (o) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178. (p) Fürstner, A.; Davies, P. W. *J. Am. Chem. Soc.* **2005**, *127*, 15024. (q) Nakamura, I.; Mizushima, Y.; Yamamoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 15022. (r) Kusama, H.; Miyashita, Y.; Takaya, J.; Iwasawa, N. *Org. Lett.* **2006**, *8*, 289. (s) Genin, E.; Toullec, P. Y.; Antoniotti, S.; Brancour, C.; Genêt, J.-P.; Michelet, V. *J. Am. Chem. Soc.* **2006**, *128*, 3112. (t) Barluenga, J.; Diéguez, A.; Fernández, A.; Rodríguez, F.; Fañanás, F. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2091. (u) Sun, J.; Conley, M. P.; Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2006**, *128*, 9705. (v) Marion, N.; Díez-González, S.; de Frémont, P.; Noble, A. R.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3647. (w) Sherry, B. D.; Maus, L.; Laforteza, B. N.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 8132. (x) Nakamura, I.; Sato, T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 4473.

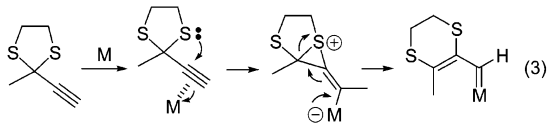
10.1021/jo0618674 CCC: $37.00
Published on Web 01/19/2007

report by Morita and Krause demonstrates that even allenyl compounds bearing a thiol group can undergo efficient reaction with AuCl as the catalyst.[5] Encouraged by those reports, we describe here the investigation of a Au-catalyzed reaction of propargylic sulfides and dithioacetals.



1,5-nucleophilic attack by ester carbonyl oxygen





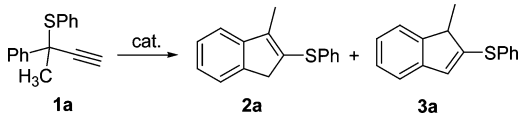
1,3-nucleophilic attack by sulfur

Results and Discussion

The propargylic sulfide **1a** was subjected to the reaction with transition-metal catalysts (Table 1). The reaction of **1a** with 5 mol % of AuCl in toluene at room temperature for 5 h afforded a 5:1 mixture of isomeric products in 63% yield (Table 1, entry 1). The structures of the products are characterized as indene derivatives **2a** and **3a** by spectral data. The reaction time could be significantly shortened when the reaction was conducted at 80 °C, with some improvements in both yield and the selectivity for **2a** (Table 1, entry 2). The addition of $AgSbF_6$ or AgOTf to the gold catalyst led to a complex mixture, and addition of PPh_3 to AuCl markedly slowed down the reaction (entries 3−5). The reaction of **1a** with 5 mol % of $AuCl_3$ gave similar yields of the indene products under the same conditions.

$PtCl_2$ was next examined. It was found that this catalyst had higher reactivity toward sulfide **1a**, as compared with the gold catalysts. The reaction of **1a** with 5 mol % of $PtCl_2$ gave a better yield but with essentially no selectivity for **2a** and **3a** (Table 1, entries 8 and 9). Other metal catalysts were also examined. $RuCl_2$(*p*-cymene) dimer was found to be less effective, while

TABLE 1. Reaction of Propargyl Sulfide 1a under Various Conditions



1a **2a** **3a**

entry	catalyst[a]	solvent	temp (°C)	time (h)	yield[b] (%)	ratio[c] (**2a**:**3a**)
1	AuCl	$PhCH_3$	25	5	63	5:1
2	AuCl	$PhCH_3$	80	1	75	10:1
3	AuCl + $AgSbF_6$	$PhCH_3$	80	1	*d*	
4	AuCl + AgOTf	$PhCH_3$	80	1	*d*	
5	AuCl + PPh_3	$PhCH_3$	80	26	30	1:1
6	$AuCl_3$	$PhCH_3$	25	3	78	3:1
7	$AuCl_3$	$PhCH_3$	80	1	85	5:1
8	$PtCl_2$	$PhCH_3$	25	30	80	1:1
9	$PtCl_2$	$PhCH_3$	80	1	97	1:1
10	$[RuCl_2(p\text{-cymene})]_2$	$PhCH_3$	80	19	30	2:1
11	$Rh_2(OCOCF_3)_4$	$PhCH_3$	80	8	trace	
12	AuCl	DCE	70	1	76	6:1
13	AuCl	MeCN	60	1	40	1:1
14	$AuCl_3$	DCE	70	1	82	5:1
15	$AuCl_3$	MeCN	60	1	50	1:1
16	$PtCl_2$	DCE	70	6	80	1:1

[a] All reactions were carried out with 5 mol % of catalyst. [b] Isolated yield after silica gel column chromatography. [c] Ratio determined by ^{1}H NMR of the crude product. [d] The reaction gave a complex mixture.

$Rh_2(OCOCF_3)_4$ gave only a trace amount of indene products (entries 10 and 11).

Finally, the effect of solvent was investigated. Switching the solvent to 1,2-dichloroethane (DCE) afforded comparable results (entries 12, 14, and 16). However, employing MeCN as the solvent resulted in diminished yields (entries 13 and 15).

Indene formations have been previously reported in the transition-metal-catalyzed reaction of propargylic esters.[3c,g] Metal carbene has been suggested to be the likely intermediate. Here, we propose a reaction pathway for the formation of **2a** and **3a** (Scheme 1).[6] As expected, the lone pair of sulfur attacks the adjacent metal-activated triple bond, resulting in the formation of a three-centered thiirenium intermediate **B**. Subsequent 1,2-migration of the thio group through **B** generates the metal carbene species **C** or **D**, which are considered to be in resonance with **E**. **E** might be viewed as a metal-stabilized allylic cation. As a result, **C** and **D** are in rapid equilibrium. From **C**, aromatic substitution by the metal carbene leads to the formal C−H insertion product **2a**.[7] The formation of **3a** suggests that a different pathway for the formal C−H insertion may also operate.[8] One possibility might be a Friedel−Crafts-type reaction of a phenyl ring with the metal-stabilized cation-like species, which leads to intermediate **F**, from which the release of the metal and the proton transfer to the *a* or *b* position generate **2a** and **3a**, respectively. Another possible pathway for the formation of **2a** and **3a** is intramolecular nucleophilic attack of the phenyl group on the vinyl metal moiety to generate intermediate **F** directly. Intramolecular nucleophilic attack of the C═C bond

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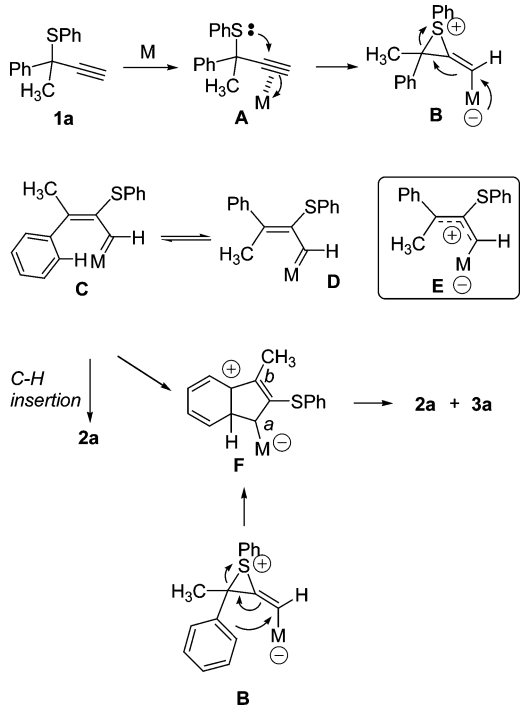
(5) Morita, N.; Krause, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 1897.

(6) For recent mechanistic discussions on Au- and Pt-catalyzed reactions of propargylic esters, see: (a) Fürstner, A.; Hannen, P. *Chem.—Eur. J.* **2006**, *12*, 3006. (b) Fehr, C.; Galindo, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 2901.

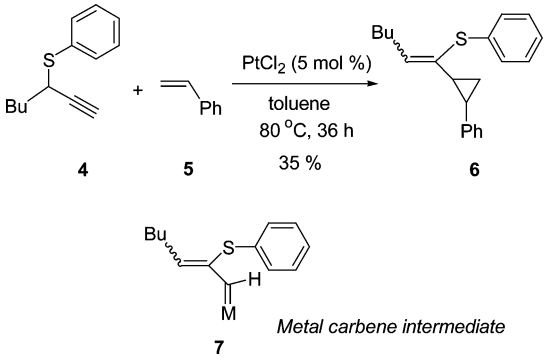
(7) For a discussion on formal insertion into the aromatic C−H by a metal carbene, see: Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669.

(8) Control experiments suggested that isomerization of **2a** and **3a** did not occur under the reaction conditions.

SCHEME 1. Mechanistic Hypothesis



SCHEME 2. Experiment on Reaction Mechanism

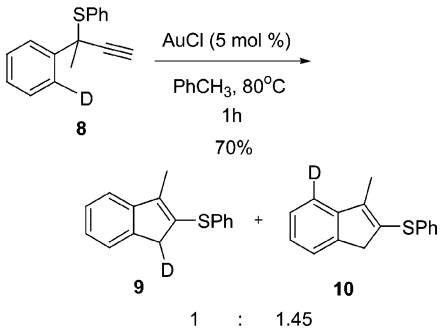


on the vinyl metal moiety in the metal-catalyzed reaction of propargylic acetates has been proposed.[3g,f]

To gain some insight into the reaction mechanism, we studied the catalytic reaction of propargyl sulfide **4**, in which the phenyl substituent of **2a** is replaced with the *n*-butyl group (Scheme 2). Unfortunately, the Au-catalyzed reaction of **4** in the presence of styrene resulted in the recovery of the starting materials. This is attributed to the low reactivity of the Au catalyst in the reaction with secondary propargyl sulfides. However, the $PtCl_2$-catalyzed reaction of **4** in the presence of styrene under identical conditions afforded a diastereomeric mixture of cyclopropane derivative **6** as a major isolated product. The formation of the cyclopropanation products is a strong evidence to indicate the generation of metal carbene **7** in such systems.[3e]

Since deuterium kinetic isotope effects have been used to probe the C−H insertion reaction of metal carbenes, we next prepared deuterium-labeled substrate **8** as a preliminary probe of primary kinetic isotope effects (Scheme 3). The AuCl-catalyzed reaction of **8** afforded a mixture of indene products **9** and **10** in a ratio of approximately 1:1.45. For metal carbene insertion into an aliphatic C−H bond, the typical kinetic isotope

SCHEME 3. Kinetic Isotopic Effects



effect has been reported in the range of 1.2−3.3.[9] However, the formal aromatic C−H insertion by a metal carbene has been known to proceed by initial cyclopropanation, followed by the hydride shift and the opening of the cyclopropyl ring.[7] This is obviously different from the direct metal carbene insertion into the aliphatic C−H bond, which has been suggested as a concerted process in most cases.[7,9,10] Consequently, the small kinetic isotope effect seen in the present work does not provide evidence to differentiate the possible pathways hypothesized in Scheme 2. More rigorous studies will be necessary to assuredly clarify this complicated mechanistic issue.

The scope of this catalytic reaction is demonstrated by a series of propargylic sulfides **1b**−**j**, as shown in Table 2. Both AuCl and $AuCl_3$ were tested for all of the sulfide substrates. The substituent on the sulfur seems to have only a marginal effect on the reaction (entries 1−5). The slow conversion in the case of the naphthyl-substituted substrate **1c** should be due to steric effects. The substrate with the alkyl substituent on the sulfur gave similar results (entry 4). On the other hand, the substituent in the alkyne moiety seems to have a significant effect on the outcome of the reaction (entries 6 and 8). In the case of **1g**, the reaction with AuCl or $AuCl_3$ proceeded slowly. In this case, the corresponding Au carbene intermediate has a methyl substitute attached to carbene carbon. The reactivity of the Au carbene is thus diminished due to the stabilizing effect of the methyl group. In the case of **1i**, the reaction with both AuCl and $AuCl_3$ gave only one product, **2i**. This may be due to the attachment of an electron-withdrawing ester group to the metal carbene, which may lead to a more carbene-like intermediate (rather than a cation-like intermediate). Formal C−H insertion should be more likely to occur from a carbene-like intermediate. The secondary sulfide was found to be less reactive under the same reaction conditions (entry 9). This is similar to the catalytic reaction of propargylic acetate.[3c]

This catalytic reaction can be extended to the sulfide with a vinyl substituent **11** (Scheme 4). In this case, the reaction

(9) (a) Demonceau, A.; Noels, A. F.; Costa, J.-L.; Hubert, A. J. *J. Mol. Catal.* **1990**, *58*, 21. (b) Wang, P.; Adams, J. *J. Am. Chem. Soc.* **1994**, *116*, 3296. (c) Sulikowski, G. A.; Lee, S. *Tetrahedron Lett.* **1999**, *40*, 8035. (d) Ishii, S.; Zhao, S.; Helquist, P. *J. Am. Chem. Soc.* **2000**, *122*, 5897.

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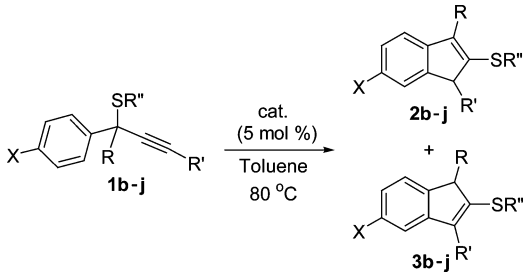
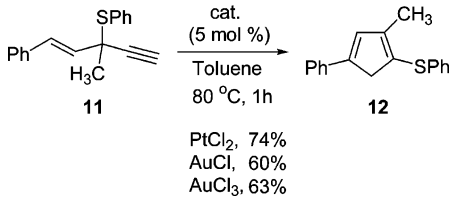
TABLE 2. AuCl- or $AuCl_3$-Catalyzed Reaction of 1b−j



entry	sulfide	catalyst	time (h)	yield[a] (%)	ratio[b] (**2**:**3**)
1	**1b**, X = R′ = H; R = CH_3	AuCl	1	56	15:1
	R″ = *o*-ClC_6H_4	$AuCl_3$	1	63	10:1
2	**1c**, X = R′ = H; R = CH_3	AuCl	34	24 (60)	10:1
	R″ = *β*-naphthyl	$AuCl_3$	34	30 (51)	5:1
3	**1d**, X = R′ = H; R = CH_3	AuCl	1	60	8:1
	R″ = benzyl	$AuCl_3$	1	75	4:1
4	**1e**, X = R′ = H; R = CH_3	AuCl	1	68	4:1
	R″ = hexyl	$AuCl_3$	1	65	3:1
5	**1f**, X = R′ = H; R = CH_3	AuCl	1	70	7:1
	R″ = $CH_2C_6H_4Cl$-*o*	$AuCl_3$	1	70	5:1
6	**1g**, X = H; R′ = R = CH_3	AuCl	25	32 (63)	*c*
	R″ = C_6H_5	$AuCl_3$	25	13 (81)	
7	**1h**, X = Br; R′ = H	AuCl	4	53	15:1
	R = CH_3; R″ = C_6H_5	$AuCl_3$	2	68	10:1
8	**1i**, X = H; R′ = CO_2Et	AuCl	16	57 (25)	>20:1[d]
	R = CH_3; R″ = C_6H_5	$AuCl_3$	16	67 (11)	>20:1
9	**1j**, X = R′ = R = H	AuCl	24	9 (32)	*c*
	R″ = C_6H_5	$AuCl_3$	24	10 (30)	

[a] Isolated yields after silica gel column chromatography. Numbers in parentheses refer to the starting material recovered. [b] Determined by ^{1}H NMR of the crude product. [c] The reaction can only give one isomer when R = R′. [d] No **3i** could be identified by crude ^{1}H NMR.

SCHEME 4. Catalytic Reaction with 11



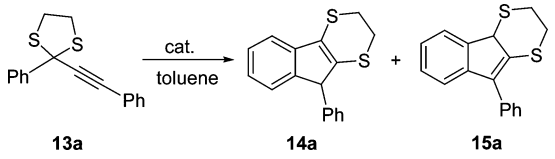
afforded a cyclopentadiene derivative **12**,[3f] which was formed through vinylic C−H insertion of the metal carbene.

After establishing that the metal carbene could be generated through the metal-catalyzed reaction of propargyl sulfide, we proceeded to investigate the reaction with propargyl dithioacetals. As shown by eq 3, it can be anticipated that propargylic dithioacetals may work in the same way as propargyl sulfide upon catalyzation with transition metals. In this case, the five-membered dithioacetal ring is expanded to a six-membered ring with the generation of vinylcarbenoids.

The investigation started with dithioacetal **13a**, as summarized in Table 3. The $PtCl_2$-catalyzed reaction gave a complicated mixture. From the crude ^{1}H NMR spectra, **15a** was identified as the major product (entry 1). To our delight, the reaction with both AuCl and $AuCl_3$ afforded **14a** as the only isomer with high isolated yields (entries 2−5). Ru(II) and Rh(II) catalysts were also tested. In both cases, most of the starting material **13a** was recovered after prolonged reaction time (entries 6 and 7).

The generality of the AuCl-catalyzed reaction of propargyl dithioacetals is demonstrated by a variety of substrates, as shown

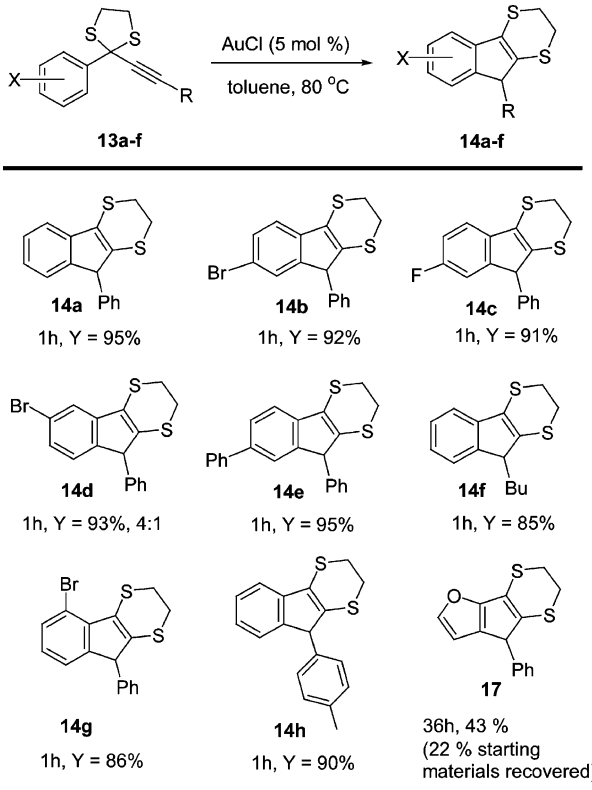
TABLE 3. Reaction of Dithioacetal 13a under Various Conditions



entry	catalyst[a]	temp (°C)	time (h)	yield[b] (%)	ratio[c] (**14**:**15**)
1	$PtCl_2$	80	23	78[d]	1:8
2	AuCl	80	1	95	1:0
3	$AuPPh_3Cl$	80	10	89	1:0
4	$AuCl_3$	80	1	92	1:0
5	AuCl	25	6	94	1:0
6	$[RuCl_2(p\text{-cymene})]_2$	80	22	*e*	
7	$Rh_2(OCOCF_3)_4$	80	22	*e*	

[a] All reactions were carried out with 5 mol % of catalyst. [b] Isolated yield after silica gel column chromatography. [c] Ratio determined by ^{1}H NMR of the crude product. [d] The product contains a small amount of an unknown impurity. [e] Starting material was recovered.

SCHEME 5. AuCl-Catalyzed Reaction of Propargyl Dithioacetals



in Scheme 5. Indene derivatives were isolated in good to excellent yields, except in the case of 2-furyl substrate **16**, in which case the reaction proceeded slowly to afford **17**. Compared to the reaction with propargyl sulfide, the Au-catalyzed reaction with propargyl dithioacetals is generally more efficient, presumably due to the rigidity of the substrate in the latter case. Moreover, since dithioacetals are easily available from the corresponding ketones,[11] this catalytic reaction provides an unique and efficient entry to the indene derivatives.

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In conclusion, we have demonstrated that a neighboring sulfur group can participate the transition-metal-catalyzed reactions of alkynes to generate a vinylcarbenoid as the reactive intermediate through 1,2-sulfur migration.[12] This result provides a new entry to these important intermediates and thus significantly expands the scope of the chemistry of alkyne-generated metal carbenes. Further studies on the detailed reaction mechanism and the application of this process in organic synthesis are underway in our laboratory.

Experimental Section

The Synthesis of Propargylic Sulfides 1a−f,h−j. The propargylic sulfides were synthesized through a catalyzed propargylic substitution reaction of propargylic alcohols with thiols. We mainly used two methods, catalysis with ZnI_2 (Method A)[13] or catalysis with PTS (*p*-toluenesulfonic acid monohydrate) (Method B).[14] The sulfides can also be synthesized by catalysis with a thiolate-bridged diruthenium complex[15] or $NaAuCl_4 \cdot 2H_2O$.[16] Recently, some other methods for preparing propargylic sulfides have appeared in literature.[17]

Phenyl-1-methyl-1-phenyl-2-propynyl Sulfide 1a. Yield 49%. **Method A:** white solid; mp 45−46 °C; IR (film) 3292, 1439, 1067, 750, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.94 (s, 3H), 2.70 (s, 1H), 7.20−7.36 (m, 8H), 7.57−7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.9, 49.2, 74.7, 86.1, 126.7, 127.4, 128.0, 128.2, 129.1, 132.3, 136.4, 141.8; EI−MS (*m*/*z*, relative intensity) 238 (M^+, 8), 223 (26), 129 (100). Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92. Found: C, 80.62; H, 5.95.

Phenyl-1,3-dimethyl-1-phenyl-2-propynyl Sulfide 1g. For this sulfide, the following procedure is followed. Under a nitrogen atmosphere, BuLi was added dropwise to a solution of phenyl-1-methyl-1-phenyl-2-propynyl sulfide **1a** (238 mg, 1 mmol) in anhydrous THF (10 mL) at −78 °C. After 1 h, CH_3I (0.13 mL, 2 mmol) was added, and the temperature was allowed to increase up to room temperature. Five hours later, saturated NH_4Cl was added, and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by a silica gel column eluted with petroleum ether to afford **1g** (91%): oil; IR (film) 2917, 1438, 1027, 749, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.89 (s, 3H), 1.91 (s, 3H), 7.19−7.34 (m, 8H), 7.56−7.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 3.8, 30.1, 49.9, 81.5, 82.9, 126.7, 127.2, 127.9, 128.1, 128.8, 132.8, 136.5, 142.9; EI−MS (*m*/*z*, relative intensity) 252 (M^+, 4), 237 (7), 143 (100), 128 (27). Anal. Calcd for $C_{17}H_{16}S$: C, 80.90; H, 6.39. Found: C, 80.91; H, 6.42.

Phenyl-1-methyl-1-styryl-2-propynyl Sulfide 11. Yield 63%. **Method B:** oil; IR (film) 3288, 1583, 1480, 1438, 744, 693 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.81 (d, J = 1.5 Hz, 3H), 3.11 (d, J = 0.3 Hz, 1H), 5.41 (d, J = 10.5 Hz, 1H), 5.99−6.03 (m, 1H), 7.21−7.34 (m, 7H), 7.36−7.41 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.7, 53.0, 82.0, 82.2, 118.6, 127.2, 127.4, 127.7, 128.6, 128.6, 132.7, 137.9; EI−MS (*m*/*z*, relative intensity) 264 (M^+, 4), 249 (5), 155 (100), 129 (13). Anal. Calcd for $C_{18}H_{16}S$: C, 81.77; H, 6.10. Found: C, 81.64; H, 6.10.

Typical Procedure for $PtCl_2$-, $AuCl_3$-, or AuCl-Catalyzed Rearrangement Reactions of 1a−j and 11. Under a nitrogen atmosphere, metal catalyst (AuCl, $AuCl_3$) (0.01mmol) and propargylic sulfide (0.2 mmol) were mixed in dry toluene, and the system was heated at 80 °C. Upon completion of the reaction as judged by TLC, solvent was removed in vacuo to give a crude residue which was purified by a silica gel column eluted with petroleum ether. Isomeric products **2** and **3** were found to be inseparable on a silica gel column.

3-Methyl-2-phenylthioindene 2a: oil; IR (film) 3067, 1476, 1461, 1439, 1024, 757, 739, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.27 (t, J = 2.1 Hz, 3H), 3.44 (d, J = 2.1 Hz, 2H), 7.16−7.37 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.7, 42.1, 119.1, 123.3, 125.3, 126.2, 126.5, 129.0, 129.3, 132.0, 136.4, 143.2, 144.0, 145.5; EI−MS (*m*/*z*, relative intensity) 238 (M^+, 44), 129 (100). Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92. Found: C, 80.55; H, 5.95.

2-Methyl-4-phenyl-1-phenylthiocyclopenta-1,3-diene 12: white solid; mp 62−63 °C; IR (film) 3053, 1476, 1440, 1373, 752, 739, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.12 (t, J = 2.1 Hz, 3H), 3.51−3.52 (m, 2H), 6.83 (s, 1H), 7.10−7.32 (m, 8H), 7.40−7.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2, 45.5, 124.9, 125.5, 127.2, 127.7, 128.6, 128.9, 130.6, 135.3, 138.3, 147.9, 149.7; EI−MS (*m*/*z*, relative intensity) 264 (M^+, 43), 249 (9), 171 (13), 155 (100). Anal. Calcd for $C_{18}H_{16}S$: C, 81.77; H, 6.10. Found: C, 81.53; H, 5.91.

The Synthesis of Propargylic Dithioacetals 13a−h and 16. The propargylic dithioacetals were prepared from the corresponding propargylic ketones and 1,2-ethanedithiol in the presence of $BF_3 \cdot Et_2O$.[11a] There are two ways to prepare the propargylic ketones, Method A by a direct coupling reaction (for the synthesis of **13a**,**f**,**h**) and[18] Method B by two-step reaction that involves first a nucleophilic addition and then oxidation (for the synthesis of **13b−e**,**g**, and **16**).

Method B. A flame-dried, three-necked flask was charged with dry THF (20 mL) and phenylacetylene (12.0 mmol). The solution was cooled to −78 °C, and *n*-BuLi (12.0 mmol, 2.0 M in hexane) was added slowly. The solution was allowed to stir for 1 h at −78 °C; then, aldehyde (10.0 mmol) in 20 mL of THF was added slowly over 20 min. The mixture was stirred for an additional 1 h at −78 °C; then, the dry ice/acetone bath was removed, and the mixture was allowed to warm to room temperature. After about 5 h, saturated NH_4Cl was added, and most of the organic solvent was then removed in vacuum. The mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by a silica gel column eluted with petroleum ether/EtOAc (20:1) to afford the corresponding propargylic alcohol.

A solution of propargylic alcohol (10.0 mmol) in CH_2Cl_2 (50 mL) was cooled to 0 °C, and MnO_2 (50.0 mmol) was added by portion. This was kept in the ice bath for another 2 h. Then, the solid was removed by filtration. The filtrate was evaporated, and the crude residue was purified by a silica gel column eluted with petroleum ether/EtOAc (100:1) to afford the propargylic ketone.

2-Phenyl-2-(2-phenylethynyl)-1,3-dithiolane 13a:[11a] yield 72%; IR (film) 1597, 1489, 1446, 756, 718, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.67−3.81 (m, 4H), 7.30−7.42 (m, 6H), 7.50−7.54 (m, 2H), 8.03−8.06 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 41.3, 62.2, 86.8, 91.0, 122.7, 127.6, 128.2, 128.3, 128.4, 131.6, 138.7; EI−MS (*m*/*z*, relative intensity) 282 (M^+, 72), 254 (65), 221 (100), 189 (54), 145 (57), 77 (20).

Typical Procedure for AuCl-Catalyzed Rearrangement Reactions of 13a−h and 16. Under a nitrogen atmosphere, AuCl (0.01

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mmol) and propargylic dithioacetal (0.2 mmol) were mixed in dry toluene, and the system was heated at 80 °C by a boil bath. The temperature was kept until the reaction was completed as judged by TLC. Removal of the solvent in vacuo gave a crude residue, which was purified by a silica gel column eluted with petroleum ether.

9-Phenyl-2,3-dihydro-1,4-dithiofluorene 14a:[19] white solid; mp 122−123 °C; IR (film) 1600, 1536, 1493, 1463, 1265, 754, 734, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.20−3.25 (m, 4H), 4.53 (s, 1H), 7.04−7.31 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.1, 27.3, 59.3, 116.7, 123.0, 123.7, 124.8, 127.0, 127.2, 128.2, 128.7, 132.5, 138.9, 143.0, 145.0; EI−MS (*m*/*z*, relative intensity) 282 (M^+, 100), 254 (53), 221 (64), 189 (6), 177 (18), 165 (8), 111 (15).

Acknowledgment. The project is generously supported by the Natural Science Foundation of China (Grant Nos. 20572002, 20521202, 20225205, 20390050) and the Ministry of Education of China.

Supporting Information Available: Synthesis of propargylic sulfides and dithioacetals, spectra data for all new compounds, X-ray structure of sulfone, cyclopropanation and kinetic isotope effect experiments, and copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0618674