unsaturated organic substrates is under investigation.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **2** and **5** (11 pages); tables of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

Regio- and Stereoselective Addition of Tantalum–1-(Alkylthio)-1-alkyne Complexes with Carbonyl Compounds[†]

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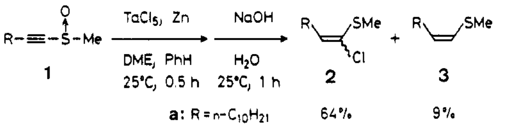
Summary: Treatment of methyl alkynyl sulfides with low-valent tantalum ($TaCl_5$ and Zn) in 1,2-dimethoxyethane (DME) and benzene produces unisolable tantalum–alkyne complexes, which react with carbonyl compounds at the 2-position of the alkenyl sulfides to give (*E*)-3-hydroxy-1-propenyl methyl sulfide derivatives in a regio- and stereoselective manner.

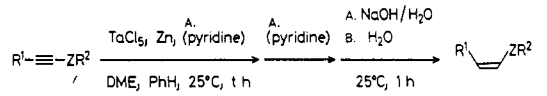
Easy access to metal complexes of functionalized alkynes would widely extend the applicability of the metal–alkyne complexes in organic synthesis.[1] Little is known about the metal complexes of hetero-substituted alkynes in contrast to dialkyl- or silyl-substituted alkynes. In 1989, however, Livinghouse and co-workers have demonstrated[1c] that zirconium complexes of alkynyl sulfides exhibit significant stabilization and that the thioalkyl group can be used to control the regiochemistry in subsequent coupling with other alkynes. We disclose herein the preparation of tantalum complexes of alkynyl sulfides and sulfones (not isolated) and cross-coupling of the tantalum complexes with carbonyl compounds under high stereocontrol.

Formation of tantalum–alkyne complexes from alkynyl sulfides[2] proceeds faster than that of tantalum–dialkylacetylene complexes.[1g] Alkenyl sulfides were produced after alkaline workup.[3] Pretreatment of low-valent tantalum with pyridine before the addition of alkynes prevented the formation of 1-chloro-1-alkenyl sulfides as byproducts. Although *Z* isomers were obtained predominantly, the *Z*/*E* selectivities of the sulfides varied with the hydrolytic conditions. Addition of 20 equiv of pyridine before alkaline workup was found to suppress the isomerization, and (*Z*)-alkenyl sulfides were obtained under high stereocontrol (Table I). Complexation of alkynyl sulfones[4] with the low-valent tantalum proceeded slowly (runs 5–7). (*Z*)-Alkenyl sulfones were produced exclusively from the corresponding alkynyl sulfones after the complexes were quenched with water. In contrast to the alkynyl sulfides and sulfones, treatment of alkynyl sulfoxides **1** with the $TaCl_5$–Zn system did not give the corresponding alkenyl sulfoxides but afforded a mixture of 1-chloro-1-alkenyl sulfides **2** and (*Z*)-alkenyl sulfides **3** (eq 1).[5]



(1)

Table I. Preparation of (*Z*)-Alkenyl Sulfides and Sulfones by Hydrolysis of the Corresponding Tantalum–Alkyne Complexes



run	R^1	ZR^2	method[a]	*t*/h	yields/%[b]	*Z*/*E*[c]
1	*n*-$C_{10}H_{21}$	SMe	A	0.75	97	98/2
2		SPh	A	1	96	93/7
3	c-C_6H_{11}	SMe	A	0.5	75	98/2
4	Ph	SMe	A	0.5	91	98/2
5	*n*-$C_{10}H_{21}$	SO_2Me	B	2.5	72[d]	100/0
6		SO_2Ph	B	22	69[d]	100/0
7	c-C_6H_{11}	SO_2Me	B	2.5	68[d]	100/0

[a] Reactions were performed on a 1.0 mmol scale at 25 °C. Method A: Two millimoles of $TaCl_5$, 3.0 mmol of zinc, and 1.0 mmol of pyridine were employed. Additional pyridine (20 mmol) was introduced to the reaction mixture before hydrolysis with a NaOH solution (15%, 2 mL). Method B: Three millimoles of $TaCl_5$ and 4.5 mmol of zinc were employed. The reaction was quenched with water (3 mL). [b] Isolated yields. [c] Geometric purity was ascertained by ^1H or ^{13}C NMR and/or capillary GLPC analysis. [d] Reference 6.

In the case of unsymmetrical alkynes, the reaction of metal–alkyne complexes with carbonyl compounds could

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[†] Dedicated to the memory of Professor John K. Stille.

(1) Some representative examples of reactions of metal–alkyne complexes with carbonyl compounds. For Zr, see: (a) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986,** *108,* 7441. Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *Ibid.* **1987,** *109,* 2544. Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988,** *88,* 1047. (b) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987,** 623. (c) Van Wagenen, B. C.; Livinghouse, T. *Tetrahedron Lett.* **1989,** *30,* 3495. For Nb, see: (d) Hartung, J. B., Jr.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989,** *111,* 5468. Pedersen, S. F. In *Abstracts of Papers,* 194th National Meeting of the American Chemical Society, at New Orleans, Fall 1987; American Chemical Society: Washington, DC, 1987; ORG 218. (e) Kataoka, Y.; Miyai, J.; Tezuka, M.; Takai, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett,* **1990,** *31,* 369. (f) Williams, A. C.; Sheffels, P.; Sheehan, D.; Livinghouse, T. *Organometallics* **1989,** *8,* 1566. For Ta, see: (g) Takai, K.; Kataoka, Y.; Utimoto, K. *J. Org. Chem.* **1990,** *55,* 1707. (h) Strickler, J. R.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990,** *9,* 266.

(2) Brandsma, L. *Preparative Acetylenic Chemistry,* 2nd ed.; Elsevier: Amsterdam, 1988; p 132.

(3) Kataoka, Y.; Takai, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990,** *31,* 365.

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(5) Deoxygenation of 1-dodecynyl methyl sulfoxide (**1a**) to the corresponding sulfide with low-valent tantalum could occur prior to the formation of a tantalum complex of the sulfoxide **1a**. Both 1-chloro-1-alkenyl sulfide **2a** and alkenyl sulfide **3a** could stem from 1-dodecynyl methyl sulfide, because (i) treatment of 1-dodecynyl methyl sulfide with $TaCl_5$ in the absence of pyridine at 25 °C for 2 h afforded 1-chlorododecenyl methyl sulfide (**2a**) in 50% yield and (ii) the yield of **2a** decreased and that of **3a** increased with increasing the amounts of low-valent tantalum.

(6) Reduction of a sulfonyl group to a sulfide took place as a side reaction.

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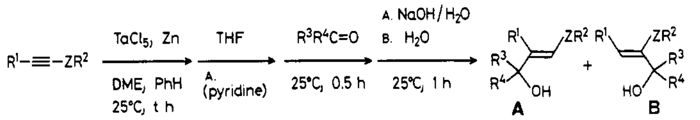
Table II. Reactions of Alkynyl Sulfides and Sulfones with Carbonyl Compounds by Means of a $TaCl_5$–Zn System

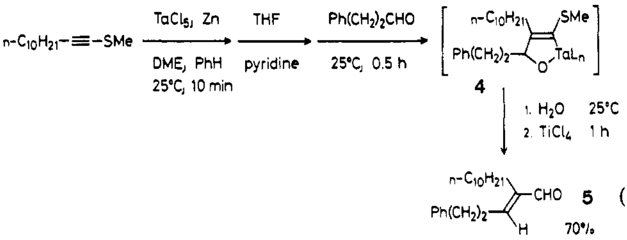


run	R^1	ZR^2	R^3	R^4	method[a]	t/h	yields/%[b]	A/B[c]
1	n-$C_{10}H_{21}$	SMe	$Ph(CH_2)_2$	H	A	0.2	73	>99/<1
2		SPh			A	0.5	85	77/23
3		SMe	c-C_6H_{11}	H	A	0.2	74	>99/<1
4			$-(CH_2)_5-$		A	0.2	77	>99/<1
5		SPh			A	0.5	75	85/15
6	c-C_6H_{11}	SMe	$Ph(CH_2)_2$	H	A	0.2	68	>99/<1
7			$-(CH_2)_5-$		A	0.2	70	>99/<1
8	Ph	SMe	$Ph(CH_2)_2$	H	A	0.5	64	>99/<1
9			$-(CH_2)_5-$		A	0.5	54	>99/<1
10	n-$C_{10}H_{21}$	SO_2Me	$Ph(CH_2)_2$	H	B	2.5	54[d]	54/46
11		SO_2Ph			B	21	43[d]	28/72
12		SO_2Me	c-C_6H_{11}	H	B	2.5	46[d]	65/35
13			$-(CH_2)_5-$		B	2.5	62[d,e]	>99/<1
14	c-C_6H_{11}	SO_2Me	$Ph(CH_2)_2$	H	B	2.5	59[d]	39/61

[a] Reactions were performed on a 1.0 mmol scale at 25 °C. Method A: Two millimoles of $TaCl_5$, 3.0 mmol of zinc, 2.0 mmol of a carbonyl compound, and 4.0 mmol of pyridine were employed. The reaction mixture was hydrolyzed with a 15% NaOH solution. See refs 7 and 8. Method B: Three millimoles of $TaCl_5$, 4.5 mmol of zinc, and 2.0 mmol of a carbonyl compound were employed. Pyridine was not added to the reaction mixture. The reaction was quenched with water (3 mL). [b] Isolated yields. [c] The isomer ratios were determined by ^1H and ^{13}C NMR analysis. [d] Reference 6. [e] Four millimoles of cyclohexanone was used.

produce two regioisomers.[1g] For example, a zirconocene–1-(methylthio)-1-alkyne complex is reported to add to a carbonyl compound to yield two regioisomeric allylic alcohols in an almost 1 to 1 ratio.[1c] In contrast, tantalum–1-(methylthio)-1-alkyne complexes were found to react with carbonyl compounds at the 2-position of the alkenyl methyl sulfide, and allylic alcohol A was produced exclusively. The results are shown in Table II.[7] Regioselectivities depended on the substituent on sulfur. Lower selectivities (A/B) were observed when 1-(phenylthio)-1-alkyne was employed (runs 2 and 5). Tantalum–alkynyl sulfone complexes added to the carbonyl compounds at both the α- and β-positions of the starting sulfones (runs 10-12 and 14). Bulkiness and the electronic nature of the substituents of alkynes influence the regioselectivities of the coupling reaction.[1g]

Acidic hydrolysis of a tantalum–1-(methylthio)-1-dodecyne complex (4) proceeded smoothly with $TiCl_4$, and an E isomer of α,β-unsaturated aldehyde 5 was produced exclusively in 70% yield (eq 2).[9]



4

5 (2)

Supplementary Material Available: Spectral and analytical data for all new compounds (8 pages). Ordering information is given on any current masthead page.

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(7) Typical Procedure: Zinc (0.20 g, 3.0 mmol) was added at 25 °C to a stirring pale-yellow solution of $TaCl_5$ (0.72 g, 2.0 mmol) in DME–benzene (1:1, 10 mL) under an argon atmosphere, and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned to greenish dark blue with a slightly exothermic process. To the mixture was added at 25 °C a solution of 1-(methylthio)-1-dodecyne (0.21 g, 1.0 mmol) in DME–benzene (1:1, 2 mL) and the whole mixture was stirred at 25 °C for 12 min. THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the mixture was stirred at 25 °C for 20 min, 3-phenylpropanal (0.27 g, 2.0 mmol) was added to the mixture, and the resulting mixture was stirred at 25 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited brown solid was removed by filtration with Hyflo Super-Cel and washed well with ethyl acetate (3 × 5 mL). Organic extracts were dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel (ethyl acetate–hexane, 1:10) gave (E)-2-decyl-1-(methylthio)-5-phenyl-1-penten-3-ol in 73% yield (0.25 g).

(8) Addition of pyridine prior to treatment of 1-alkynyl sulfides retarded the reaction of the formed tantalum complexes with carbonyl compounds, and unreacted alkenyl sulfides remained. Therefore, pyridine was not used before addition of the alkynyl sulfides. This procedure caused, however, substantial formation (15–20%) of 1-chloro-1-alkenyl sulfides 2. See text.

(9) Trost, B. M.; Stanton, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4018.