Formal Hydroallylation of Carbon-Carbon Triple Bonds *via* Tantalum-Alkyne Complexes. Stereoselective Preparation of 1,4-Dienes

Kazuhiko Takai,*†† Masashi Yamada, Hidetoshi Odaka, Kiitiro Utimoto,* Takeshi Fujii,† and Isao Furukawa*†
Division of Material Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606-01
†*Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Tanabe-cho, Tsuzuki-gun, Kyoto 610-03*

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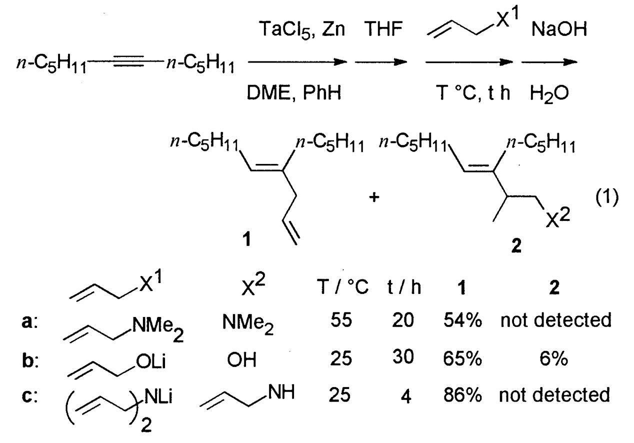
Treatment of tantalum-alkyne complexes with lithium salts of allylic alcohols in DME-benzene-THF (1:1:1) at 25 °C for several hours gives 1,4-dienes stereoselectively in good to excellent yields.

There are two major pathways for preparation of stereodefined 1,4-alkadienes by formal hydroallylation of alkynes: Allylmetalation followed by hydrolysis[1] and hydrometalation followed by trapping with allylic electrophiles.[2] We disclose here another allylmetalation approach to the formal *cis*-hydroallylation of acetylenes using tantalum-alkyne complexes.[3-5]

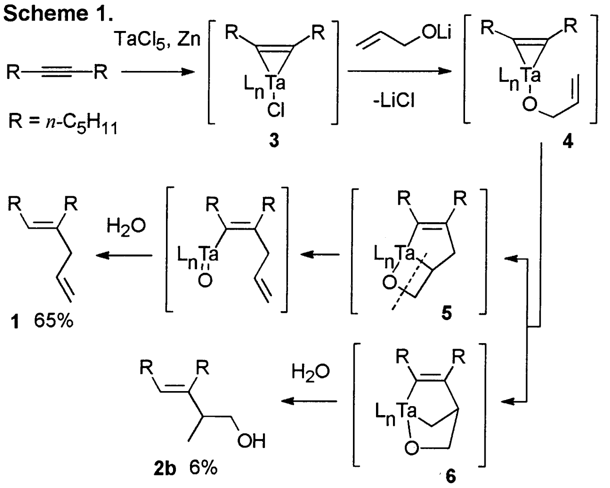
In contrast to the insertion of carbon-oxygen double bonds into tantalum-alkyne complexes,[4a] insertion of carbon-carbon double bonds was quite limited.[3b,4c] For example, treatment of 1-dodecene with a tantalum-6-dodecyne complex at 55 °C for 20 h resulted in quantitative recovery of 1-dodecene. Allyl dodecyl ether was also recovered almost quantitatively under the same reaction conditions.[3] However, *N,N*-dimethylallylamine was found to react with the tantalum complex at 55 °C and 1,4-diene **1**, a formal *cis*-hydroallylation product of 6-dodecyne, was obtained in 54% yield (eq. 1). The results suggest that it is necessary to bring the double bonds close to the tantalum for insertion of carbon-carbon double bonds and, in addition, that the dialkylamino group is more effective than the alkoxy group in the case of tantalum-alkyne complexes.[6,7]



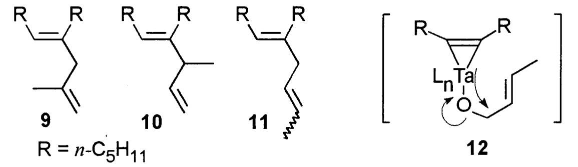
	X^1	X^2	T / °C	t / h	1	2
a:	NMe$_2$	NMe$_2$	55	20	54%	not detected
b:	OLi	OH	25	30	65%	6%
c:	NLi)$_2$	NH	25	4	86%	not detected

The insertion was accelerated by using a lithium salt of allyl alcohol,[4c] and the 1,4-diene **1** was produced in 65% yield after stirring at 25 °C for 2 h. Terminal alcohol **2b** derived from regioisomeric insertion was produced in 6% yield. A similar insertion reaction was observed with a lithium salt of diallylamine. Formation of 1,4-diene **1** and alcohol **2b** using the lithium salt of allyl alcohol could be explained by a plausible mechanism shown in Scheme 1. Insertion of an olefinic bond of allyl alcohol into the tantalum-carbon bond of the complex **4** forms two oxatantalabicycloheptene intermediates **5** and **6**. Deoxygenative ring-opening of oxatantalacyclobutane ring of the intermediate **5** followed by hydrolysis provides **1**.[8] Internal coordination of allylalkoxide to the tantalum accelerates the insertion and enhances the regioselectivity (**5**/**6** = **1**/**2b**) of the insertion.[9]

Scheme 1.

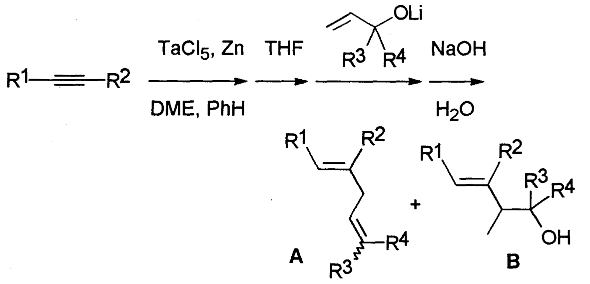


The proposed mechanism suggests that substituents on the olefinic carbons could retard the insertion. Indeed, the reaction between the tantalum-6-dodecyne complex **3** and a lithium alkoxide derived from 2-methyl-2-propen-1-ol (**7**) or crotyl alcohol (**8**) did not proceed at 25 °C and required heating at 50 °C. The desired 1,4-dienes **9** and **10** were obtained in 43% and 33% yields, respectively, by the reaction of the lithium alkoxides of **7** and **8** with the tantalum complex **3** at 50 °C for 20 h. In the case of crotyl alcohol (**8**), regioisomeric 1,4-diene **11** was obtained in 9% yield (*E*/*Z* = 88 / 12)[10] which could be produced through the mechanism shown in **12**.[4d]



Additional steric demand at 1-position of allylic alcohols did not disturb the insertion and one of the regioisomeric 1,4-dienes **A** was produced selectively in 81-89% yields (runs 2-4 and 8). The stereoselectivity of the newly formed disubstituted double bonds increased from 1/1 to 3/1, when size of the substituents R^3 became bigger, Me < c-C$_6$H$_{11}$ < *t*-Bu. Silyl-substituted allylic alcohols can be prepared from allyl alcohol *via* the retro-Brook rearrangement (runs 5-7).[11] The *E*/*Z* ratios of the produced terminal alkenylsilanes were in the range from 63/37 to 69/31.

Table 1. Regioselectivity of Reactions between Tantalum-Alkyne Complexes and Carbonyl Compounds [a]



Run	R^1	R^2	R^3	R^4	Time / h	$\mathbf{A}^b$ / %	E/Z^c	$\mathbf{B}^b$ / %
1	n-C_5H_{11}	n-C_5H_{11}	H	H	30	65[d]	----	6
2			Me	H	3	81[d]	52 / 48	5
3			c-C_6H_{11}	H	2	87	66 / 34	<1
4			t-Bu	H	2	83	76 / 24	<1
5			Me_3Si	H	2	67[e]	69 / 31	<1
6			t-$BuMe_2Si$	H	2	76[f]	64 / 36	<1
7			$PhMe_2Si$	H	2	56[f]	63 / 37	<1
8			Me	Me	2	89	----	<1
9	Me_3Si	n-$C_{10}H_{21}$	H	H	2	70[g]	----	14[g]
10			Me	Me	2	86[g,h]	----	<1[g]

[a] Reactions were conducted on a 1.0 mmol scale. See ref. 12. [b] Isolated yields. [c] The *E*/*Z* ratios of disubstituted olefins were determined by ^1H NMR analysis. [d] $TaCl_5$ (2.0 mmol), Zn (3.0 mmol), and lithium alkoxide (4.0 mmol) were employed. [e] Trimethylsilyl-substituted alkoxide was prepared from allyl alcohol in one-pot. [f] Silyl-substituted alkoxide were prepared from the corresponding silyl allyl ethers. [g] Regioisomers with respect to acetylenic carbons was not observed. [h] Pyridine (10 mmol) was added.

In the case of a trimethylsilyl acetylene, a new carbon-carbon bond was formed at the carbon bearing the alkyl group, not the silyl group, exclusively (runs 9 and 10).[4b] The high regioselectivity could stem from approach of the olefinic bond from the less hindered side of the tantalacyclopropene. In the case of 2-methyl-3-buten-2-ol (run 10), 10 equiv. of pyridine were added to prevent isomerization of the alkenylsilane moiety of the product.

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References and Notes

[††] Present address: *Department of Applied Chemistry, Faculty of Engineering, Okayama University, Tsushima, Okayama 700.*

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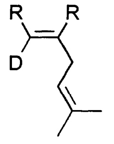
12 *Typical procedure* (Table 1, run 8): A tantalum-6-dodecyne complex was prepared at 50 °C from $TaCl_5$ (0.48 g, 1.2 mmol), zinc (0.12 g, 1.8 mmol), and 6-dodecyne (0.17 g, 1.0 mmol) in DME-benzene (1:1, 8 mL) as reported.[4a] THF (4 mL) was added at 25 °C to the mixture and the mixture was stirred at 25 °C for 15 min. A solution of a lithium salt of 2-methyl-3-buten-2-ol (0.21 g, 2.4 mmol) in DME-benzene-THF (7.2 mL, 1:1:1) was prepared separately by using BuLi (a 1.6 M hexane solution, 1.5 mL, 2.4 mmol). To the mixture of the tantalum-6-dodecyne complex was added the solution of the lithium alkoxide. The resulting mixture was stirred at 25 °C for 2 h. After usual alkaline workup,[4a] the mixture was purified by column chromatography on silica gel (hexane only) to give 0.21 g (89% yield) of the desired 1,4-diene **13**. When the reaction mixture was quenched with an NaOD-D_2O solution, deuterium was introduced in 90% selectivity (**13**-*d*, 81% chemical yield) at one of the olefinic positions attached to tantalum.



R = n-C_5H_{11}
13-*d*