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Alkoxy-Directed Insertion of Carbon−Carbon Double Bonds into Tantalum−Alkyne Complexes. Chemo- and Stereoselective Addition of Alkenyl Groups to Olefins

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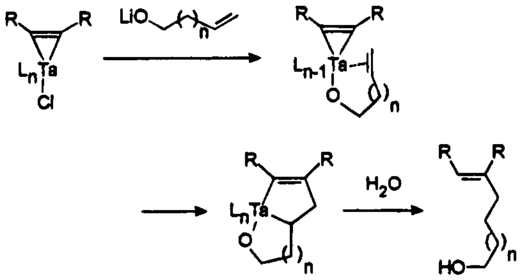
Summary: Chemo- and stereoselective addition of alkenyl groups at terminal positions of olefins is accomplished by the reaction between tantalum−alkyne complexes and terminal olefins having adjacent hydroxyl groups.

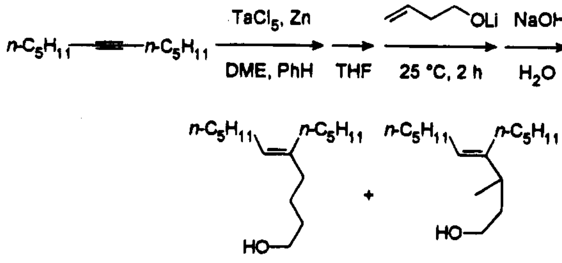
Formation of carbon−carbon bonds at olefinic positions is one of the fundamental methods to construct carbon frameworks.[1] We disclose herein chemo- and stereoselective insertion of olefinic bonds into tantalum−alkyne complexes using adjacent hydroxyl groups as handles.

Tantalum−alkyne complexes employed here can be easily prepared by mixing acetylenes with low-valent tantalum derived from $TaCl_5$ and zinc.[2,3] The formed tantalum−alkyne complexes react with carbonyl compounds[4a−c] and hydrazones[4d] to produce the corresponding heterosubstituted tantalacyclopentenes, which are hydrolyzed to yield (*E*)-allylic alcohols and hydrazines, respectively. However, insertion of carbon−carbon double bonds into the tantalum−carbon bonds does not take place even in the intramolecular case,[2b,5] which shows sharp contrast to zirconocene−alkyne complexes.[6] Reactivity of unsaturated bonds with the tantalum−alkyne complex decreased substantially in the order $>C{=}O$ > $>C{=}N-$ > $>C{=}C<$ in our hands.[7] Because the tantalum−alkyne complexes derived by using the $TaCl_5$−Zn system do not possess a bulky Cp ligand, the complexes could have five or more coordination sites which could be occupied by halogens and ethereal solvents.[8] Thus, carbon−carbon double bonds could be brought close to the tantalum by ligand exchange with the halogen when lithium alkoxides tethered to the olefinic double bonds were employed (eq 1).[3b] We have found that the insertion into the tantalum−alkyne complexes can be accelerated by using such ligands.



(1)

Treatment of a tantalum−6-dodecyne complex with lithium 3-buten-1-olate in DME−benzene−THF (1:1:1) at 25 °C for 3 h gave alcohols **1a** and **1b** in 80% yield after alkaline workup (eq 2). Regioselectivity of the products **1a**/**1b** was 98/2. Prior coordination of the tantalum−alkyne complex with the hydroxyl group of the homoallyl alcohol both facilitates the insertion and controls the regiochemistry. Similarly, lithium 4-penten-1-olate gave alcohols **2a** and **2b** in a ratio of 94/6 in 72% combined yield (Table 1, run 2). Further homologated lithium alkoxide, lithium 5-hexen-1-olate, produced a mixture of the two adducts **3a** and **3b** in only 4% combined yield even after stirring at 50 °C for 20 h. Distance from the hydroxyl group affects significantly the yield and regioselectivity.



(2)

1a 80% (98/2) **1b**

While the additional steric demand of a secondary and a tertiary alcohol affects neither the yield nor the selectivity of the reaction (runs 7 and 10), the reactivity decreased substantially when substitution at the olefinic carbons increased. Only 4−24% yields of adducts were

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(1) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ed.; Pergamon Press: Oxford, 1991; Vol. 4, Semmelhack, M. F., Ed., especially Chapter 3-2, pp 571−583 (Hegedus, L. S.), Chapter 4-1 and 4-2, pp 715−831 (Curran, D. P.); Chapter 4-3, pp 833−863 (Heck, R. F.), Chapter 4-4, pp 865−911 (Knochel, P.).

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(3) For other tantalum−alkyne complexes, see: (a) Labinger, J. A.; Schwartz, J.; Townsend, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4009. (b) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. *J. Inorg. Chem.* **1981**, *20*, 387. (c) van der Heijden, H.; Gal, A. W.; Pasman, P.; Orpen, A. G. *Organometallics* **1985**, *4*, 1847. (d) Arnold J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037. (e) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067. (f) Herberich, G. E.; Savvopoulos, I. *J. Organomet. Chem.* **1989**, *362*, 345. (g) Carnahan, E. M.; Lippaard, S. J. *J. Am. Chem. Soc.* **1992**, *114*, 4166.

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(5) To our knowledge, only ethylene inserts into a tantalum−alkyne complex as an olefinic component. See ref 3b.

(6) (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *Ibid.* **1987**, *109*, 2544. (c) RajanBabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128.

(7) The following factors can account for the decrease of reactivity: decrease of polarization, decrease of the number of unshared lone pairs, and increase of steric hindrance by substituents.

(8) The tantalum−alkyne complexes derived by using $TaCl_5$ and zinc have not been isolated. Because the complexes showed similar reactivity toward phthalaldehyde[8b] as does the Pedersen's niobium−alkyne complexes derived from acetylenes and $NbCl_3(DME)_2$,[8a] we assume that the structure of tantalum−alkyne complexes employed here could be analogous to the niobium complexes. See: (a) Hartung, J. B., Jr.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 5468. (b) Kataoka, Y.; Miyai, J.; Tezuka, M.; Takai, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 369.

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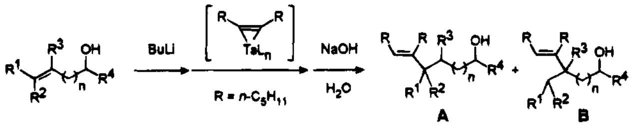
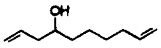
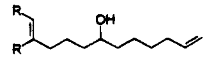
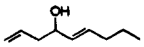
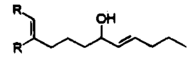
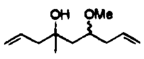
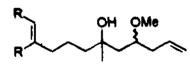
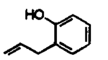
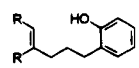
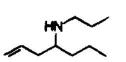
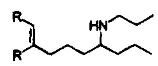
Table 1. Reactions between a Tantalum−6-Dodecyne Complex and Olefinic Alcohols[a]



run	R^1	R^2	R^3	R^4	n	temp / °C	time / h	yield /%[b]	A / B[c]
1	H	H	H	H	1	25	2	80	98 / 2 (**1a**) (**1b**)
2	H	H	H	H	2	25	2	72	94 / 6 (**2a**) (**2b**)
3	H	H	H	H	3	50	20	4	(85 / 15) (**3a**) (**3b**)
4	n-C_6H_{13}	H	H	H	1	50	20	24	>99 / <1
5	H	n-C_6H_{13}	H	H	1	50	20	17	98 / 2
6	H	H	n-C_6H_{13}	H	1	50	20	4	>99 / <1
7	H	H	H	n-C_5H_{11}	1	25	3	82	97 / 3

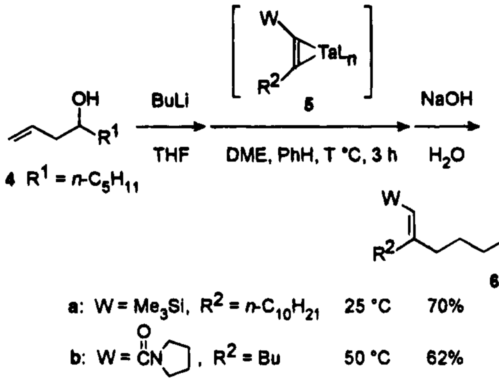
run	olefin	major product A	temp / °C	time / h	yield /%	A / B
8			25	3	84	98 / 2
9			25	3	83	>99 / <1
10	 d		25	3	85[e]	>99 / <1
11			25	3	86	>99 / <1
12			50	3	70[f]	>99 / <1

[a] Reactions were performed on a 1.0 mmol scale. See experimental section of supplementary material. [b] Isolated yields. [c] Isomer ratios were determined by ^1H NMR analysis. [d] A mixture of two diastereomers (56/44) was employed. [e] Diastereomer ratio was 50/50. [f] Crude product was acetylated with Ac_2O and Et_3N, and the yield indicated is for its acetamide.

obtained with disubstituted olefins even after treatment at 50 °C for 20 h (runs 4−6). Anionic groups derived from a phenol and a secondary amine were effective as handles to promote the insertion process (runs 11 and 12). In contrast, neutral functional groups, such as ester, ether, and *tert*-amine groups, were not effective as handles; acetates and benzyl ether of the alcohols were recovered unchanged in 86% and 96% yields, respectively.

Anchimeric coordination of the hydroxyl group is indispensable to promote the insertion.[9,10] In addition, substitution at the olefinic carbons also affects the reaction rate. These features enabled us to accomplish site−selective addition of an alkenyl group to olefins (runs 8−10). The olefinic bonds apart from hydroxyl groups remained intact during the carbon−carbon bond formation at the nearer terminal positions.

Tantalum−alkyne complexes of functionalized acetylenes can also be prepared similarly with the low-valent tantalum ($TaCl_5$−Zn).[4c] When 1-(trimethylsilyl)-1-dodecyne was employed, a new carbon−carbon bond was formed at the carbon bearing the alkyl group, not the silyl group, exclusively (eq 3). The high regioselectivity



(3)

could stem from approach of the olefinic bond from the less hindered side of the tantalum−alkyne complex **5a**. Tantalum−α,β-acetylenic amide complex **5b** also reacted with **4** to yield **6b** in 62% yield (eq 3). The other regioisomers with respect to the olefinic double bond or the acetylene were not observed.

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Supplementary Material Available: Experimental procedure and spectroscopic data (IR, ^1H NMR, ^{13}C NMR, MS) for new compounds (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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