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Reaction of Tantalum–Alkyne Complexes with Hydrazones. Stereoselective Synthesis of (*E*)-Allylic Hydrazines

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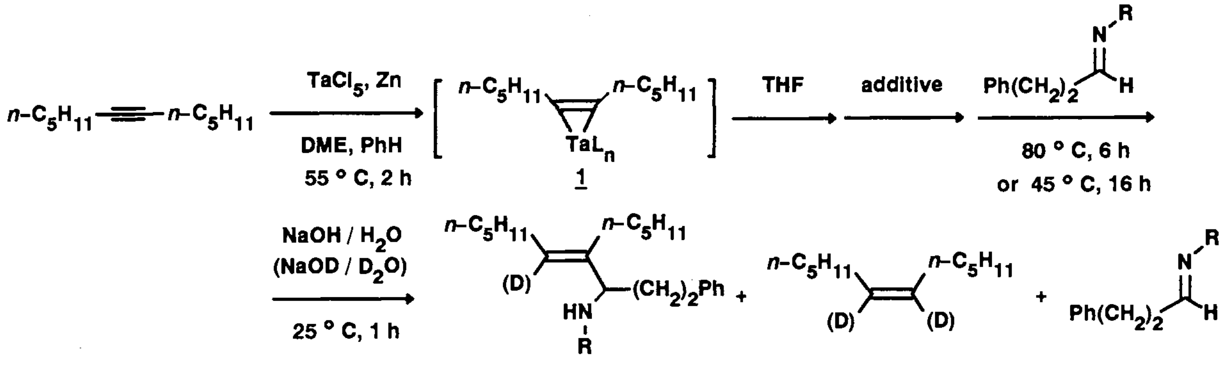
Treatment of tantalum–alkyne complexes with dimethylhydrazones by the assistance of Me_3Al in a mixed solvent of DME, benzene, and THF at 45 °C for 16 h gives (*E*)-allylic hydrazines stereoselectively.

The addition of organometallic compounds to carbon–nitrogen double bonds constitutes an important method for the preparation of amines.[1–3] We have reported regio- and stereoselective synthesis of (*E*)-allylic alcohols by the reaction between tantalum–alkyne complexes and carbonyl compounds.[4] In order to apply the reaction to the synthesis of allylic amines, we employed imines and its derivatives (oximes, hydrazones) in place of the carbonyl compounds.[5]

Treatment of tantalum–6–dodecyne complex **1** with *N*-(3-phenylpropylidene)isopropylamine (**2**) at 80 °C for 6 h gave 6-dodecene, hydrolyzed product of the complex **1**, in 70% yield after workup (Table 1, run 1). *O*-Methyloxime of 3-phenylpropanal (**3**) did not react with the complex **1** (run 2). In contrast, *N,N*-dimethylhydrazone **4** reacted with the complex **1** at 80 °C to give allylic hydrazine **6** in 25% yield, along with many byproducts derived by the reaction of **4** with low-valent tantalum.[6] Diphenylhydrazone **5** was recovered quantitatively under the same conditions. Excess amounts of the low-valent tantalum reduced the yield of the adduct **6** (run 4). Thus, 1.2 equiv. of tantalum and 1.8 equiv. of zinc were employed and a mixture of the low-valent tantalum and 6-dodecyne were heated at 55 °C to form the complex. (*E*)-Allylic hydrazine **6** was produced exclusively,[7] as expected from the insertion of a hydrazone double bond into the tantalum–carbon bonds of the alkyne complexes.

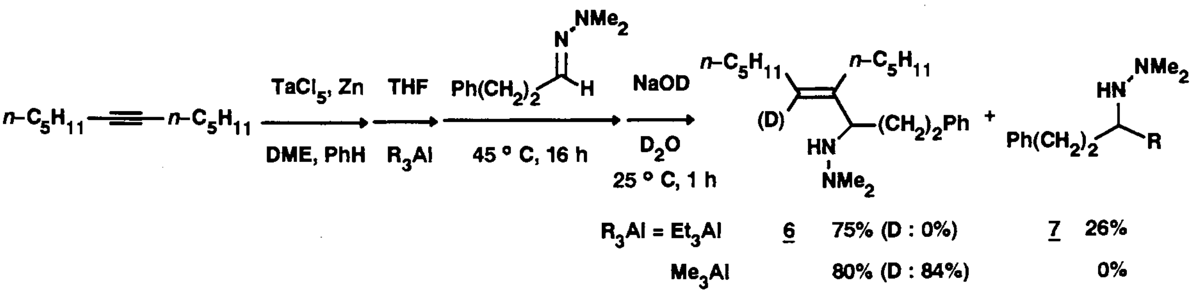
Yields of allylic hydrazine depended on additives before addition of a hydrazone. The coupling reaction between the tantalum–alkyne complex and a hydrazone did not proceed without addition of THF. Addition of Lewis bases such as pyridine and TMEDA suppressed the reaction. On the contrary, Lewis acid, in particular, organoaluminum compounds accelerate the reaction markedly (runs 6–8). Although both organoaluminum compounds Et_3Al and Me_3Al were effective for the addition reaction, the two compounds differed in two points (Eq. 1). First, while addition of ethyl group to the hydrazone **4** proceeded smoothly, the product between the hydrazone **4** and Me_3Al was not obtained. Second, deuterium could not be introduced at the olefinic position of **6** by quenching with NaOD–D_2O in the case of Et_3Al, which shows sharp contrast to the reaction with Me_3Al.

Table 1. Reactions of a Tantalum-6-Dodecyne Complex with Imine Derivatives[a)]



Run	R	Additive[b)]	Yield/%[c,d)]	Unreacted 6-dodecene / %[c,d)]	Recov. $Ph(CH_2)_2CH{=}NR$ / %[c)]
1	*i*-Pr [**2**]	none	<1	70	-
2	OMe [**3**]	none	<1	73	92
3	NMe_2 [**4**]	none	25 [**6**]	52	54
4		none	11[e)]	35	34
5		Et_3B	8	52	53
6		Et_2AlCl	43 (0)	32 (74)	0
7		Et_3Al	75[f)] (0)	8 (0)	20
8		Me_3Al	80 (84)	12 (30)	31
9		Me_3Ga	46 (91)	11 (47)	38
10	NPh_2 [**5**]	none	0	78	100

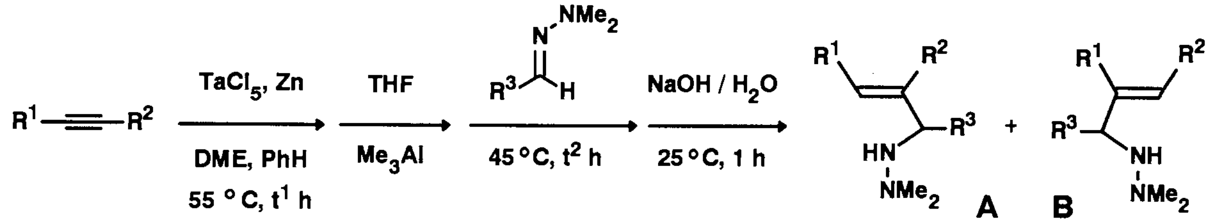
a) The reactions were conducted on 1.0 mmol scale. 1.2 mol of $TaCl_5$, 1.8 mol of zinc, 2.0 mol of an imine derivative were employed per mole of an alkyne. b) Reaction was conducted either at 80 °C for 6 h without any additive or at 45 °C for 16 h with an additive. c) Isolated yields. d) Content of deuterium at olefinic position(s) after quenching with NaOD / D_2O are shown in parentheses. e) Two mmol of $TaCl_5$ and 3.0 mmol of zinc was employed. Tantalum-6-dodecyne complex was produced at 25 °C for 30 min. f) Three mmol of hydrazone **4** was used. See Ref. 8.



(1)

Two regioisomeric allylic hydrazines were produced in the case of unsymmetrical alkynes (Table 2, runs 5–8). The isomeric ratios of allylic hydrazine A/B were not so sensitive to the bulkiness of the substituents R^1 and R^2 compared to those of the reactions with aldehydes (runs 5 and 7).[4a)] Electronic effect is also a directing factor of the regiochemistry. The reaction between hydrazone **4** and a tantalum–alkyne complex derived

Table 2. Reactions between Tantalum-Alkyne Complexes and Hydrazones in the Presence of $Me_3Al^{a)}$

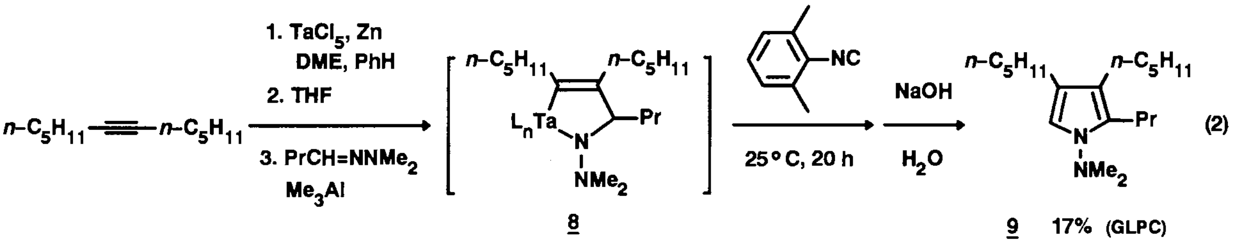


Run	R^1	R^2	R^3	t^1/h	t^2/h	$Yield^{b)}$/%	A / $B^{c)}$	Unreacted $alkene^{d)}$/%	Recov. hydrazone/%
1	$n-C_5H_{11}$	$n-C_5H_{11}$	$Ph(CH_2)_2$	2	16	$80^{e)}$ [**6**]	-	12	31
2			$c-C_6H_{11}$	2	16	71	-	21	24
3			(*E*)-PrCH=CH	2	16	32	-	26	48
4			(cyclohexanone)	2	16	5	-	45	62
5	$c-C_6H_{11}$	$n-C_6H_{13}$	$Ph(CH_2)_2$	3	16	64	51 / 49	10	23
6	Ph	$n-C_6H_{13}$	$Ph(CH_2)_2$	4	16	76	44 / 56	9	22
7	Me_3Si	$n-C_{10}H_{25}$	$Ph(CH_2)_2$	3	16	57	80 / 20	21	33
8	MeS	$n-C_{10}H_{25}$	$Ph(CH_2)_2$	0.2	26	69	>99 / <1	$-^{f)}$	33

a) The reactions were conducted in 1.0 mmol scale. 1.2 mol of $TaCl_5$ and 1.8 mol of zinc were employed per mole of an alkyne. b) Isolated yields. c) The regioisomer ratios (**A**/**B**) were determined by ^1H NMR. d) (*Z*)-$R^1CH=CHR^2$. e) See typical procedure. f) 1-Chloro-1-undecenyl methyl sulfide was obtained in 10% yield.

from methylthio-substituted alkyne afforded one of the regioisomer **A** exclusively in 69% yield (run 8).[4b)]

Insertion of carbon monoxide and isocyanide into tantalum-carbon bond of intermediate oxatantalacyclopentene proceeds efficiently to give substituted furans.[9)] Similar insertion of isocyanide into the azatantalacyclopentene **8** also took place. Although yields were not optimized yet, 2,3,4-trisubstituted *N*-amino pyrrole **9** was produced in 17% GLPC yield (Eq. 2).[10)]



Typical Procedure for the Reaction between an Alkyne and an *N*,*N*-Dimethylhydrazone by Means of a $TaCl_5$-Zn System: To a stirred pale yellow solution of $TaCl_5$ (0.43 g, 1.2 mmol) in DME-benzene (1:1, 6 mL) was added zinc (0.12 g, 1.8 mmol) at 25 °C under an argon atmosphere and the mixture was stirred at 25 °C for 40 min. The color of the mixture turned greenish dark blue with slightly exothermic process. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in DME-benzene (1:1, 2 mL) and the mixture was heated at 50 °C for 2 h. THF was added to the reaction mixture at 25 °C and the mixture was stirred at 25 °C for 15 min. A hexane solution of Me_3Al (1.0 M, 2.0 mL, 2.0 mmol) and 3-phenylpropanal dimethylhydrazone (0.35 g, 2.0 mmol) were added successively and the whole mixture was heated at 45 °C for 16 h. Aqueous NaOH solution (15%, 1.2 mL) was added slowly at 0 °C and the mixture was stirred at 25 °C for an additional 1 h. The deposited solid was removed by filtration with Hyflo-Super Cel^R and washed with ethyl acetate (3x5 mL). The filtrate and washings were dried over Na_2SO_4 and concentrated. Purification of the crude product by column chromatography on silica gel (ethyl acetate-hexane, 1:10) gave 0.28 g (80% yield) of allylic hydrazine **6**.11)

References

1) K. Harada, "The Chemistry of the Carbon-Nitrogen Double Bond," ed by S. Patai, Interscience, London (1970), Chap. 6.
2) For some representative examples using hydrazones, see: D. Enders, H. Schubert, and C. Nübling, *Angew. Chem., Int. Ed. Engl.*, **25**, 1109 (1986); D. A. Claremon, P. K. Lumma, and B. T. Phillips, *J. Am. Chem. Soc.*, **108**, 8265 (1986); S. E. Denmark, T. Weber, and D. W. Piotrowski, *ibid.*, **109**, 2224 (1987).
3) For some representative examples of reactions between metal-alkyne (or -alkene) complexes and nitriles, see: S. A. Cohen and J. E. Bercaw, *Organometallics*, **4**, 1006 (1985); S. L. Buchwald, B. T. Watson, and J. C. Huffman, *J. Am. Chem. Soc.*, **109**, 2544 (1987); J. R. Strickler and D. E. Wigley, *Organometallics*, **9**, 1665 (1990).
4) a) K. Takai, Y. Kataoka, and K. Utimoto, *J. Org. Chem.*, **55**, 1707 (1990); b) K. Takai, J. Miyai, Y. Kataoka, and K. Utimoto, *Organometallics*, **9**, 3030 (1990).
5) For the synthesis of allylic amine derivatives mediated by zirconocene-imine complexes, see: S. L. Buchwald, B. T. Watson, M. W. Wannamaker, and J. C. Dewan, *J. Am. Chem. Soc.*, **111**, 4486 (1989); M. Jensen and T. Livinghouse, *ibid.*, **111**, 4495 (1989); R. B. Grossman, W. M. Davis, and S. L. Buchwald, *ibid.*, **113**, 2321 (1991).
6) Hydrazones were smoothly consumed with the low-valent tantalum to give complex mixtures.
7) Stereochemistry was confirmed by comparison with an authentic sample derived from the corresponding allylic alcohol.4a)
8) Because of fast consumption of the hydrazone **4** to form ethyl adduct **7**, 3.0 equiv. of hydrazone was employed.
9) K. Takai, M. Tezuka, Y. Kataoka, and K. Utimoto, *J. Org. Chem.*, **55**, 5310 (1990).
10) **9**: Bp 94 °C (bath temp, 0.20 Torr); IR (neat): 2952, 2924, 2854, 1731, 1455, 1377, 1269, 1018, 928, 787 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8-1.0 (m, 9H), 1.2-1.7 (m, 14H), 2.3-2.6 (m, 6H), 2.73 (s, 6H), 6.57 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 14.3, 22.6, 23.9, 24.7, 26.2, 26.2, 29.8, 31.7, 32.1, 48.0, 107.0, 114.8, 121.1, 129.0. Anal. Found: C, 77.77; H, 12.58; N, 9.39%. Calcd for $C_{19}H_{36}N_2$: C, 78.02; H, 12.41; N, 9.58%.
11) **6**: Bp 138 °C (bath temp, 0.27 Torr); IR (neat): 2924, 2854, 2804, 2760, 1730, 1467, 1456, 895, 743, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, J=6.4 Hz, 6H), 1.2-1.5 (m, 12H), 1.6-2.2 (m, 7H), 2.39 (s, 6H), 2.4-2.7 (m, 2H), 3.20 (dd, J=7.1, 7.4 Hz, 1H), 5.36 (t, J=7.1 Hz, 1H), 7.1-7.4 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.1, 22.5, 22.6, 27.7, 28.5, 29.5, 29.6, 31.7, 32.5, 32.5, 34.9, 48.1, 63.9, 125.5, 128.1, 128.2, 128.3, 139.9, 142.7; MS *m/z* (rel intensity): 344 (M^+, 18), 117 (17), 91 (50), 59 (100). Anal. Found: C, 80.22; H, 11.91; N, 8.07%. Calcd for $C_{23}H_{40}N_2$: C, 80.17; H, 11.70; N, 8.13%.

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