Preparation, Structural Characterization, and Reactions of Tantalum-Alkyne Complexes $TaCl_3(R^1C{\equiv}CR^2)L_2$ (L_2 = DME, Bipy, and TMEDA; L = Py)

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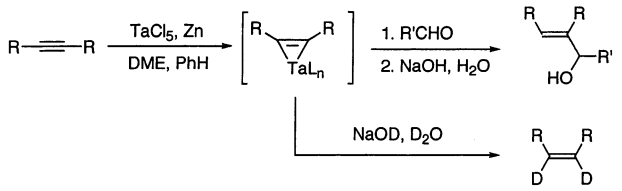
Tantalum-alkyne complexes with the general formula $TaCl_3(R^1C{\equiv}CR^2)$(dme) (**1a**, $R^1 = R^2$ = Et; **1b**, $R^1 = R^2 = n$-C_5H_{11}; **1c**, R^1 = Ph, R^2 = Me; **1d**, $R^1 = R^2$ = Ph; DME = 1,2-dimethoxyethane) were synthesized by treatment of the corresponding alkynes with a low-valent tantalum derived by reduction of tantalum pentachloride with zinc powder in a mixed solvent of toluene and DME. The DME ligand can be replaced by 2 equiv of pyridine to afford the corresponding dipyridine complexes $TaCl_3(R^1C{\equiv}CR^2)(py)_2$ (**2a**, $R^1 = R^2$ = Et; **2b**, $R^1 = R^2 = n$-C_5H_{11}; **2c**, R^1 = Ph, R^2 = Me; **2d**, $R^1 = R^2$ = Ph). Additionally, the reaction of **1a** with the bidentate nitrogen ligands bipyridine and *N*,*N*,*N*′,*N*′-tetramethyethylenediamine (= TMEDA) gave $TaCl_3$(EtC≡CEt)(bipy) (**3**) and $TaCl_3$(EtC≡CEt)(tmeda) (**4**), respectively. The η^2- and 4e-coordination mode of an alkyne with a large contribution of a metalacyclopropene canonical structure was revealed by spectroscopic methods (NMR and IR) and crystallographic analyses of **1a**, **1c**, **2a**, and **4**. The reactivies of the tantalum-3-hexyne complexes **1a**, **2a**, **3**, and **4** toward 3-phenylpropanal were investigated. Only the pyridine complex **2a** reacted with a stoichiometric amount of the aldehyde to afford the corresponding allylic alcohol in 77% yield upon hydrolysis. The reaction proceeded via an oxatantalacyclopentene species.

Introduction

Alkyne complexes of transition metals have attracted considerable attention in organometallic chemistry.[1−3] Characterization and theoretical calculations of various alkyne complexes have revealed their structures and the bonding nature of the metal−alkyne bond. Most monomeric metal−alkyne complexes have η^2-alkyne ligands, and the structure of the metal−alkyne fragment is best described as a metalacyclopropene structure.[4−6] These metal−η^2-alkyne complexes react with unsaturated organic molecules, such as aldehydes and nitriles, and the reaction involves the insertion of the unsaturated organic molecule into a metal−carbon bond of the η^2-alkyne complexes to afford a ring-expanded metalacycle complex.[7] These transformations of transition metal η^2-alkyne complexes have been applied to stoichiometric organic transformation with titanium,[8,9] zirconium,[10,11] and niobium[12,13] as the central metal. In 1990, we reported that allylic alcohols are synthesized from alkynes and aldehydes with a low-valent tantalum (Scheme 1).[14−16] In these reactions, the formation of tantalum-η^2-alkyne complexes and the insertion of carbonyl groups into the tantalum−carbon bonds have been postulated. The formation of the tantalum-η^2-alkyne complexes has been supported experimentally

Scheme 1



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(1) Caffyn, A. J. M.; Nicholas, K. M. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. A., G, W., Eds.; Pergamon: NewYork, 1995; Vol. 12, p 685.
(2) Schore, N. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. A., G, W., Eds.; Pergamon: New York, 1995; Vol. 12, p 703.
(3) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.
(4) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; John Wiley & Sons: New York, 2001.
(5) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.
(6) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.
(7) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. A., G, W., Eds.; Pergamon: New York, 1995; Vol. 12, p 741.
(8) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696.
(9) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835.
(10) Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755.
(11) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124.
(12) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551.
(13) Hartung, J. B.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 5468.
(14) Takai, K.; Kataoka, Y.; Utimoto, K. *J. Org. Chem.* **1990**, *55*, 1707.
(15) Kataoka, Y.; Miyai, J.; Tezuka, M.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1992**, *57*, 6796.
(16) Kataoka, Y.; Miyai, J.; Oshima, K.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1992**, *57*, 1973.

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Table 1. $^{13}C\{^1H\}$ NMR and IR Data for Tantalum-Alkyne Complexes

complex	$^{13}C\{^1H\}$ NMR δ (ppm)	IR (ν C≡C) cm^{-1}	ref
1a	256.0	1622	this work
1b	253.6	1686	this work
1c	242.0, 256.4	1672	this work
1d	244.2	1699	this work
2a	256.4	1640	this work
2b	253.8	1634	this work
2c	256.2, 243.7	1650	this work
2d	244.2	1643	this work
3	260.7	*a*	this work
4	256.1	1675	this work
$CpTaMe_2(ArC{\equiv}CAr)$[c]	239.4	*b*	31
$CpTaMe(ArC{\equiv}CAr)(\eta^2\text{-}MeC{=}N\textit{t}\text{-}Bu)$[c]	199.68	*b*	31
$LTa(EtC{\equiv}CEt)Cl$[d]	237.81	*b*	33
$LTa(PrC{\equiv}CPr)Cl$[d]	237.01	*b*	23
$(DIPP)_3Ta(PhC{\equiv}CSiMe_3)$[e]	224.4, 226.0	*b*	28
$(DIPP)_3Ta(PhC{\equiv}CPh)$[e]	216.2	1580	21
$(EtC{\equiv}CEt)Ta(=NAr)(DIPP)(py)_2$[e]	188.4	1592	19
$Tp^{Me2}TaCl_2(PhC{\equiv}CMe)$[f]	226.8, 269.3	*b*	18
$Tp^{Me2}TaMe_2(PhC{\equiv}CMe)$[f]	234.7, 262.3	*b*	18

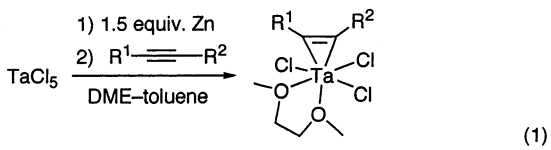
[a] Not observed. [b] Not given in the literature. [c] Ar = *p*-tolyl. [d] L = 2,6-$[ArN(SiMe_3)CH_2]_2NC_5H_3$ (Ar =2,6-$^i Pr_2C_6H_3$). [e] DIPP = 2,6-diisopropylphenoxide. [f] Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate.

by the formation of a vicinal dideuterated *cis*-alkene after quenching a reaction mixture of alkyne and the low-valent tantalum with alkaline D_2O.[14,17]

In 1999, Hierso and Etienne isolated the tantalum-η^2-alkyne complex $TaCl_3(PhC{\equiv}CMe)(dme)$, which was prepared by our low-valent tantalum methodology.[18] They characterized the complex by ^1H NMR and elemental analysis; however, there have been no reports to date on the crystallographic study of the tantalum-η^2-alkyne complexes with the general formula $TaCl_3(RC{\equiv}CR')(dme)$. In this paper, we present a detailed synthetic method for $TaCl_3(RC{\equiv}CR')(dme)$, and their molecular structures are characterized by an X-ray crystallographic analysis. The reactivities of these complexes toward nitrogen donor ligands or aldehydes are also described.

Results and Discussion

Synthesis and Characterization of $TaCl_3$(alkyne)(dme) Complexes. Tantalum-alkyne complexes with the general formula $TaCl_3(R^1C{\equiv}CR^2)(dme)$ (**1a**, $R^1 = R^2$ = Et; **1b**, $R^1 = R^2 = n\text{-}C_5H_{11}$; **1c**, R^1 = Ph, R^2 = Me; **1d**, $R^1 = R^2$ = Ph; DME = 1,2-dimethoxyethane) were prepared by the reaction of an in situ generated low-valent tantalum species with the corresponding alkynes in modest yields (eq 1). For example, the reduction of



(1)

1a : $R^1 = R^2$ = Et
1b : $R^1 = R^2 = n\text{-}C_5H_{11}$
1c : R^1 = Ph, R^2 = Me
1d : $R^1 = R^2$ = Ph

tantalum pentachloride with an excess amount of zinc powder in a mixed solvent of toluene and DME afforded a low-valent tantalum species. Treatment of the in situ generated low-valent tantalum with an equimolar amount of 3-hexyne at 50 °C for 8 h gave **1a** in 65% yield. During the reaction, the color of the reaction mixture gradually turned from dark green to reddish brown. The yield of **1a** depended strongly on the solvent, and a hydrocarbon solvent, such as toluene and benzene, was necessary in order to suppress a drastic exothermic reaction between tantalum pentachloride and DME. Thus, toluene was added to tantalum pentachloride before slowly adding DME to the resulting suspension. Complexes **1b**−**d** were prepared in a manner similar to **1a**. All alkyne complexes decomposed upon exposure to air.

NMR and IR spectral data and elemental analyses of the complexes **1a**−**d** revealed their structures. The ^1H NMR spectrum of **1a** displayed the two methyl signals of the DME ligand at δ 3.13 and 3.59 and the methylene signals as two sets of multiplet peaks at δ 3.10−3.17. The dissymmetric signal pattern of DME suggests that one of the two oxygen atoms of DME coordinates to the tantalum atom in a *trans* position to the alkyne ligand and the other in a *cis* position, and hence the three chloride ligands occupy meridional positions.[19] The complexes **1b**−**d** exhibited essentially the same ^1H NMR spectra as **1a**.

In general, an alkyne ligand coordinates to a metal center as two-electron or four-electron donor molecules. The four-electron donation has been observed for electron-deficient organometallic complexes.[5] The most informative data for the coordination mode of the alkyne ligand are their ^{13}C chemical shift values.[20] The ^{13}C NMR signals for the alkyne carbon atoms of **1a**−**d** appeared at a lower field (δ 242.0−256.4) than those of the reported η^2-alkyne complexes of tantalum having a cyclopentadienyl or aryloxy ligand (δ 188.4−239.4) (Table 1). It should be noted that the alkyne carbon of Tp^{Me2} tantalum-η^2-alkyne complexes also resonated at ca. 260 ppm.[18] These spectroscopic data indicate that the alkyne ligand donates four electrons to the electron-

(17) Kataoka, Y.; Takai, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 365.
(18) Hierso, J.-C.; Etienne, M. *Eur. J. Inorg. Chem.* **2000**, 839.
(19) Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3860.
(20) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

Table 2. Crystal Data and Structure Refinement for 1a, 1c, 2a, and 4

	1a	1c	2a	4
formula	$C_{10}H_{20}Cl_3O_2Ta$	$C_{13}H_{18}Cl_3O_2Ta$	$C_{16}H_{20}Cl_3N_2Ta$	$C_{12}H_{26}Cl_3N_2Ta$
fw	459.57	493.59	527.65	485.66
cryst dimens, mm	0.30 × 0.40 × 0.50	0.50 × 0.30 × 0.20	0.50 × 0.20 × 0.10	0.40 × 0.30 × 0.20
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group (No.)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
a (Å)	7.406(2)	7.105(3)	14.406(3)	7.75(1)
b (Å)	15.822(3)	12.729(5)	8.881(2)	14.13(1)
c (Å)	7.068(1)	18.788(9)	16.330(2)	15.93(2)
α (deg)	96.56(2)			
β (deg)	108.53(2)	93.69(6)	114.62(1)	93.92(5)
γ (deg)	78.70(2)			
V (Å^3)	768.7(3)	1695(1)	1899.2(8)	1739(3)
Z	2	4	4	4
ρ (calcd) (g cm^{-3})	1.985	1.933	1.845	1.854
μ (cm^{-1})	76.45	69.39	61.98	67.57
F(000)	440	944	1016	944
diffractmeter	AFC7R	AFC7R	AFC7R	RAXIS IV
radiation (d, Å)	Mo Kα (= 0.71069 Å)			
$2\theta_{max}$	55.0	55.0	55.0	58.7
no. of reflns measd	total: 3836 unique: 3832 R_{int} = 0.038	total: 4398 unique: 4161 R_{int} = 0.089	total: 4839 unique: 4508 R_{int} = 0.041	total: 3507 unique 3471
no. of reflns obsd ($I > 2\sigma(I)$)	3271	2962	2962	2915
no. of variables	146	172	199	163
refln/param ratio	22.40	24.19	22.65	21.29
R1(F) ($I > 2\sigma(I)$)	0.032	0.046	0.047	0.078
R1(F^2) (all data)	0.086	0.087	0.083	0.114
wR2(F^2) (all data)	0.213	0.123	0.147	0.209
GOF	1.10	1.19	1.25	1.74

deficient metal center.[3,20,21] In addition, the IR absorption bands for the metal-coordinated carbon−carbon bonds of **1a**−**d** appeared at 1622−1699 cm^{-1}, which are larger wavenumbers than those of aryloxytantalum complexes, 1580 cm^{-1} for $(DIPP)_3Ta(PhC{\equiv}CPh)$ (DIPP = 2,6-diisopropylphenoxide)[21] and 1592 cm^{-1} for $(EtC{\equiv}CEt)Ta(=NAr)(DIPP)(py)_2$ (Ar = 2,6-diisopropylphenyl),[19] and are comparable to those of trichloroniobium-η^2-alkyne complexes, 1684 cm^{-1} for $NbCl_3(PhC{\equiv}CPh)(thf)_2$[22] and 1692 cm^{-1} for $NbCl_3(PhC{\equiv}CMe)(thf)_2$.[22] Although the coordination geometries of the η^2-alkyne unit of **1a** and **1c** are unsymmetrical in the solid state (vide infra), the ^{13}C resonances of these η^2-alkyne carbons are observed as a singlet peak. These equivalent signals can be accounted for by the fact that the η^2-alkyne unit rotates rapidly on a tantalum−*trans*-oxygen axis on the NMR time scale.[23]

Most of the tantalum-alkyne complexes synthesized to date have bulky ligands such as Cp* and aryloxy ligands that stabilize alkyne complexes.[24−29] In contrast, the alkyne complexes **1a**−**d** contain no such bulky ligands and have substitutionally labile chloride ligands. Thus, these complexes are a useful starting material for preparing new tantalum complexes having an alkyne ligand. One example is the preparation of $Tp^{Me2}TaCl_3(PhC{\equiv}CMe)$ from **1c** and KTp^{Me2}.[18]

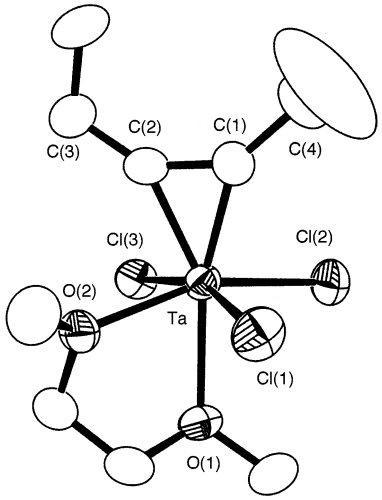


Figure 1. ORTEP drawing of complex **1a** with the numbering scheme. Selected bond distances (Å) and angles (deg) are given in Table 3.

The solid state molecular structures of **1a** and **1c** were determined by single-crystal X-ray crystallographic analyses. Table 2 provides a listing of the crystal data and refinement data. Figure 1 shows an ORTEP diagram of **1a**, and selected bond distances and angles are listed in Table 3. Orientation of the 3-hexyne ligand for **1a** is depicted in Figure 2. For the complex **1a**, the tantalum atom has a distorted octahedral geometry in which 3-hexyne occupies one corner *trans* to O(1) of the DME ligand. The 3-hexyne ligand coordinates in an η^2-fashion to the tantalum center as a formal four-electron donor ligand and is best described as a tantalacyclopropene structure.[29] The coordination geometry around the tantalum center is essentially the same as that

(21) Strickler, J. R.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 266.
(22) Cotton, F. A.; Shang, M. *Inorg. Chem.* **1990**, *29*, 508.
(23) Guèrin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 3154.
(24) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.
(25) Kwon, D.; Curtis, D. *Organometallics* **1990**, *9*, 1.
(26) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387.
(27) Belmonte, P. A.; Clock, F. G. N.; Theopold, K. H.; Shroch, R. R. *Inorg. Chem.* **1984**, *23*, 2365.
(28) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.
(29) Curtis, M. D.; Real, J.; Kwon, D. *Organometallics* **1989**, *8*, 1644.
(30) Takai, K.; Ishiyama, T.; Yasue, H.; Nobunaka, T.; Itoh, M.; Oshiki, T.; Mashima, K.; Tani, K. *Organometallics* **1998**, *17*, 5128.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1a, 1c, 2a, and 4

	1a	1c	2a	4
Ta−Cl(1)	2.383(2)	2.396(2)	2.417(3)	2.303(4)
Ta−Cl(2)	2.386(2)	2.377(2)	2.394(3)	2.375(3)
Ta−Cl(3)	2.417(2)	2.409(2)	2.408(3)	2.293(4)
Ta−O(1)	2.355(6)	2.300(6)		
Ta−N(1)			2.410(9)	2.66(1)
Ta−O(2)	2.196(5)	2.216(6)		
Ta−N(2)			2.275(9)	2.286(9)
Ta−C(1)	2.046(9)	2.047(9)	2.04(1)	2.18(1)
Ta−C(2)	2.102(7)	2.053(9)	2.07(1)	2.19(1)
C(1)−C(2)	1.39(1)	1.31(1)	1.31(2)	1.33(2)
Cl(1)−Ta−Cl(2)	96.38(8)	96.92(10)	96.2(1)	88.2(1)
Cl(2)−Ta−Cl(3)	89.54(7)	88.73(9)	88.5(1)	92.8(1)
Cl(3)−Ta−O(2)	84.0(1)	86.2(2)		
Cl(3)−Ta−N(2)			86.2(2)	87.8(3)
Cl(1)−Ta−O(2)	83.7(1)	81.7(2)		
Cl(1)−Ta−N(2)			84.2(2)	85.2(3)
Cl(1)−Ta−Cl(3)	160.85(8)	161.34(9)	162.4(1)	164.8(1)
Cl(2)−Ta−O(2)	157.8(1)	157.3(2)		
Cl(2)−Ta−N(2)			162.1(2)	156.0(3)
Cl(1)−Ta−O(1)	79.8(1)	80.5(2)		
Cl(1)−Ta−N(1)			80.8(2)	81.1(3)
Cl(1)−Ta−C(1)	89.0(2)	85.7(3)	85.7(3)	88.7(3)
Cl(1)−Ta−C(2)	107.1(2)	105.4(2)	107.7(3)	110.0(5)
C(1)−Ta−C(2)	39.1(3)	37.3(4)	37.1(4)	35.5(4)
O(1)−Ta−O(2)	71.7(2)	72.6(2)		
N(1)−Ta−N(2)			79.4(3)	74.5(4)
C(1)−C(2)−C(3)	142.9(9)	138.0(9)	143(1)	135(1)

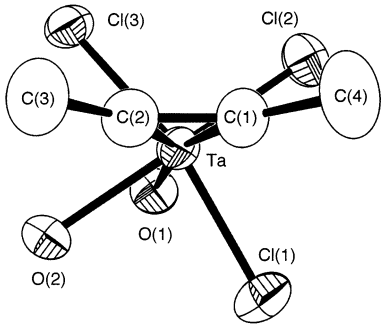


Figure 2. Schematic drawing of the coordination geometry around the tantalum atom of **1a**.

observed for $TaCl_3(dme)(PhCH{=}NCH_2Ph)$.[30] The plane consists of 3-hexyne carbons, C(1) and C(2), and the tantalum center roughly bisects the Cl(1)−Ta−Cl(2) and Cl(3)−Ta−O(2) angles. The dihedral angles of (C(3)−C(2)−Ta−O(2) and C(3)−C(2)−Ta−Cl(3) are 38(1)° and 45(1)°, respectively. The bond distances of Ta−C(1) (2.046(9) Å), Ta−C(2) (2.102(7) Å), and C(1)−C(2) (1.39(1) Å) and the angles of C(1)−C(2)−C(3) (142.9(9) Å) and C(2)−C(1)−C(4) (140.6(7) Å) are comparable to those found for tantalum-η^2-alkyne complexes (Table 4).[23,31−34] The distance of Ta−O(1) (2.355(6) Å) is much longer than that of Ta−O(2) (2.196(5) Å). The long Ta−O(1) distance can be attributed to the strong electron-donating property (strong *trans* influence) of the 3-hexyne group. The molecular structure of the 1-phenyl-1-propyne analogue **1c** is essentially the same as that of **1a** (Figure 3). The Ta−O(1) distance of **1c** (2.300(6) Å) is slightly shorter than that of **1a**, presumably due to the electron-withdrawing phenyl substituent on the alkyne fragment.

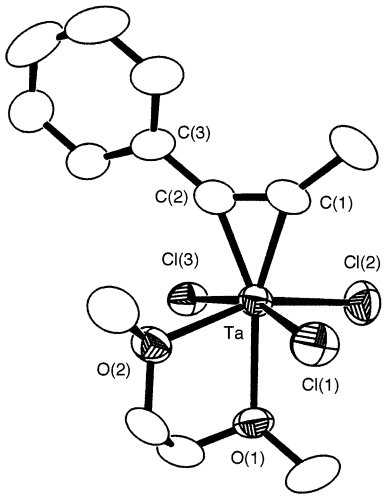


Figure 3. ORTEP drawing of complex **1c** with the numbering scheme. Selected bond distances (Å) and angles (deg) are given in Table 3.

Ligand Exchange Reactions between Complexes 1 and Nitrogen Donor Molecules. The ligand exchange reaction of **1a** with THF in toluene at room temperature proceeded rapidly within a few minutes. However, a complex mixture of unidentified products was obtained, which is consistent with the observation that no alkyne complex was obtained from a reaction of low-valent tantalum and an alkyne in a mixed solvent of toluene and THF. On the other hand, the DME ligand of **1a**−**d** was readily replaced by nitrogen donor ligands such as pyridine, bipyridine, and *N*,*N*,*N*′,*N*′-tetramethylenthylenediamine (= TMEDA). The ligand replacement reaction of **1a** with 2 equiv of pyridine in toluene at room temperature for 30 min afforded $TaCl_3(EtC{\equiv}CEt)(py)_2$ (**2a**) as red crystals in 42% yield. Other pyridine complexes $TaCl_3(R^1C{\equiv}CR^2)(py)_2$ (**2b**, $R^1 = R^2 = n\text{-}C_5H_{11}$; **2c**, R^1 = Ph, R^2 = Me; **2d**, $R^1 = R^2$ = Ph) were prepared in a similar manner. Moreover, complex **2a** was prepared directly by the simple addition of 3-hexyne to a low-valent tantalum generated by reduction of tantalum pentachloride with zinc in the presence of 10 equiv of pyridine in toluene. The coordinated pyridine was found to be labile, as an exchange reaction between $TaCl_3(EtC{\equiv}CEt)(C_5D_5N)_2$ (**2a**-d_{10}) and pyridine in $C_6D_5CD_3$ was observed. A similar rapid ligand exchange of the pyridine ligand on the tantalum atom was reported for $Ta(=NCR_3)Cl_3(py)_2$.[35] The reaction of **1a** with the bidentate ligands bipyridine and TMEDA afforded more stable alkyne complexes $TaCl_3(EtC{\equiv}CEt)L_2$ (**3**, L_2 = bipyridine; **4**, L_2 = TMEDA) in 49% and 61% yield, respectively. The ^{1}H NMR spectrum of **4** showed two singlet signals at δ 2.36 and 2.74 due to two magnetically nonequivalent methyl groups of TMEDA. This indicates that the TMEDA ligand coordinates in a bidentate fashion to the tantalum atom and that the coordination geometry around the tantalum atom is essentially the same as that of **1**. In the ^{13}C NMR spectral data for **3** and **4**, the chemical shift values of the alkyne carbons were observed at δ 260.7 and 256.1,

(31) Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. M. *Organometallics* **1990**, *9*, 66.
(32) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *20*, 2352.
(33) Guèrin, F.; McConville, D. H.; Vittal, J. J.; Yap, C. A. P. *Organometallics* **1998**, *17*, 1290.
(34) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1991,** *10*, 118.
(35) Korolev, A. V.; Rheingold, A. L.; Williams, D. S. *Inorg. Chem.* **1997,** *36*, 2647.

Table 4. Selected Bond Distances and Angles for Tantalacyclopropene Fragments of Tantalum-η^2-Alkyne Complexes

complex	Ta−C	C(1)−C(2)	∠C(1)−Ta−C(2)	ref
1a	2.046(9), 2.102(7)	1.39(1)	39.1(3)	this work
1c	2.047(9), 2.053(9)	1.31(1)	37.3(4)	this work
2a	2.07(1), 2.04(1)	1.31(2)	37.1(4)	this work
4	2.18(1), 2.19(1)	1.33(2)	35.5(4)	this work
CpTaMe(ArC≡CAr)Me(CN*t*-Bu)[a]	2.09(1), 2.11(1)	1.30(1)	*b*	31
Ta(PhC≡CPh)Cl_4(py)$^-$	2.069(8), 2.066(8)	1.325(12)	*b*	32
Ta(*n*-PrC≡C*n*-Pr)(BDPP)[c]	2.062(7), 2.085(7)	1.287(11)	*b*	23
Ta(PhC≡CC(*n*-Pr)=C(*n*-Pr)CH=CHPh)(BDPP)[c]	2.075(14), 2.030(12)	1.30(2)	*b*	33
Ta(PhC≡CPh)$(DIPP)_3$[d]	2.070(3), 2.076(3)	1.346(5)	37.9(1)	34
$Tp^{Me2}TaMe_2$(PhC≡CMe)[e]	2.061(5), 2.063(5)	1.322(7)	*b*	18

[a] Ar = *p*-tolyl. [b] Not given in the literature. [c] BDPP = 2,6-$(ArNCH_2)_2$-NC_5H_3; Ar = 2,6-diisopropylphenyl. [d] DIPP = 2,6-diisopropylphenoxide. [e] Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate.

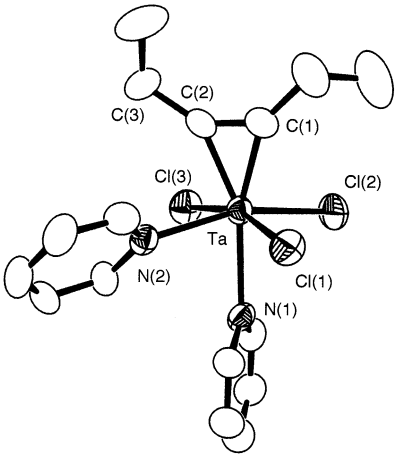
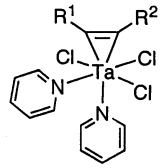
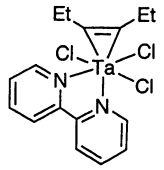


Figure 4. ORTEP drawing of complex **2a** with the numbering scheme. Selected bond distances (Å) and angles (deg) are given in Table 3.

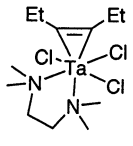
respectively, indicating that the alkyne ligand donates four electrons to the tantalum center.[18]



2a : $R^1 = R^2$ = Et
2b : $R^1 = R^2 = n\text{-}C_5H_{11}$
2c : R^1 = Ph, R^2 = Me
2d : $R^1 = R^2$ = Ph



3



4

The pyridine complex **2a** (Figures 4 and 5) and TMEDA complex **4** (Figure 6) were further characterized by crystallographic studies. Selected bonds distances and angles of **2a** and **4** are listed in Table 4. The molecular structure of **2a** was found to have the same geometry as the DME complexes **1a** and **1c**. The tantalum atom of **2a** is surrounded by the 3-hexyne ligand, two nitrogen atoms of two pyridine ligands, and three chloride atoms located at meridional positions.

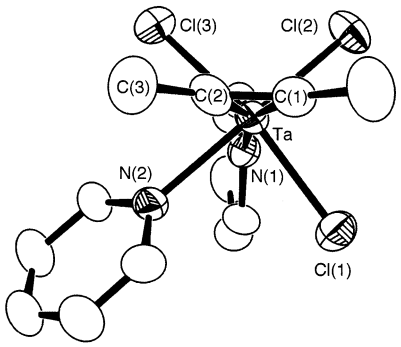


Figure 5. Schematic drawing of the coordination geometry around the tantalum atom of **2a**.

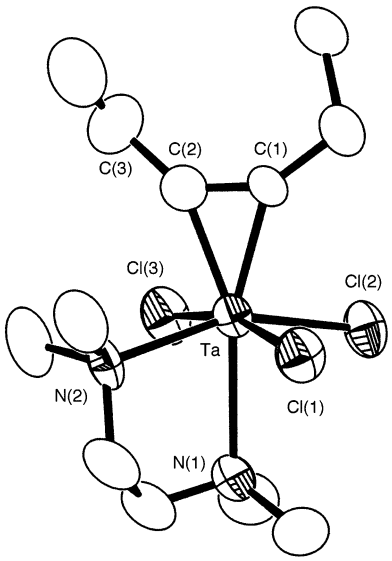
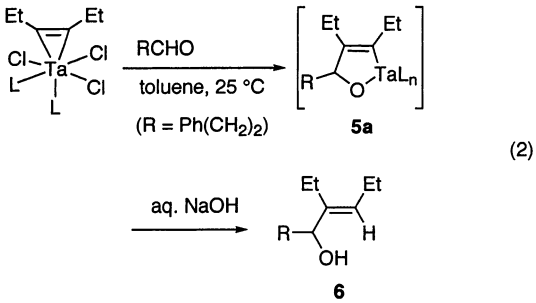


Figure 6. ORTEP drawing of complex **4** with the numbering scheme. Selected bond distances (Å) and angles (deg) are given in Table 3.

The 3-hexyne ligand coordinates to the tantalum nearly orthogonally to the *trans*-pyridine ring, and the C(1)−C(2)−Ta plane intersects the Cl(1)−Ta−Cl(2) and Cl(3)−Ta−N(2) angles. The *trans* influence of the alkyne ligand in **2a** elongated the bond distance of Ta−N(1) (2.410(9) Å) more than that of Ta−N(2) (2.275(9) Å). The chelating coordination of the TMEDA ligand somewhat deviates the geometry of **4** from that of **2a**. On the other hand, in **4**, the Ta−N(1) bond length (2.66(1) Å) *trans* to the 3-hexyne ligand is considerably longer than that of Ta−N(2) (2.286(9) Å). Thus, the N(2) atom of **4** coordinates weakly to the tantalum center.

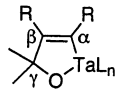
To elucidate the effect of the ligand on the reactivity of the tantalum-η^2-alkyne complex, the reactions of the tantalum-3-hexyne complexes **1a**, **2a**, **3**, and **4** with 3-phenylpropanal were examined by addition of an equimolar amount of the aldehyde to a toluene solution of the tantalum complex, followed by hydrolysis with an aqueous NaOH solution.

When the bis(pyridine) complex **2a** was used, 3-phenylpropanal was completely consumed and the allylic alcohol **6** was obtained in 77% yield. No organic byproducts were observed in this reaction. On the other hand, in the case of bidentate diamine complexes **3** and **4** and the DME complex **1a**, the allylic alcohol **5** was not obtained. Complex **3** did not react with the aldehyde, and the aldehyde was recovered in 80% yield. When **4** reacted with the aldehyde, **4** was completely consumed at 25 °C within 2 h, although compound **6** was obtained in only 4% yield and many uncharacterized organic products were formed. The reaction of **1a** with the aldehyde at 25 °C within 30 min afforded many organic products including 1,3-diene, (3*E*,5*E*)-4,5-diphenyl-1,8-diphenyl-3,5-octadiene (9% yield). The formation pathway for the 1,3-diene was deduced from our previous report for the reaction of an alkyne and a $NbCl_5$-Zn reagent.[16] Thus, only the tantalum-alkyne complexes bearing two pyridine ligands, **2a**, cleanly reacted with the aldehyde to afford the corresponding allylic alcohol **6** in good yield. These findings are consistent with our previous report that pyridine is an indispensable additive for the preparation of the allylic alcohol in high yield in the in situ reaction of the tantalum-alkyne complexes with carbonyl compounds in a mixed solvent of benzene and DME.[16] In addition, the formation of the allylic alcohol from the tantalum-η^2-alkyne complexes strongly suggests that the reaction proceeds via an oxatantalacyclopentene complex **5a**, which is generated by the insertion of a carbonyl group of the aldehyde into the tantalum−carbon bond of the tantalacyclopropene fragment.



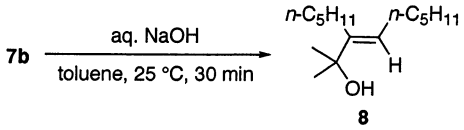
(2)

All attempts to isolate the oxatantalacyclopentene complex **5a** failed due to its thermal instability. Therefore, we characterized the complex in solution by ^{1}H and ^{13}C NMR spectroscopies. For the complex derived from 3-phenylpropanal or benzaldehyde, no signals were observed, despite using various experimental conditions. On the other hand, the corresponding oxatantalacyclopentene fragment was observed when **2a** was treated with acetone in $C_6D_5CD_3$ at 25 °C. The reaction proceeded almost quantitatively to afford **7a**. The ^{1}H NMR spectra of **7a** at 263 K displayed a singlet peak at δ 1.13, which was assigned to the methyl protons of the acetone part. Two triplet signals at δ 0.82 and 1.48 were due to



7a: R = Et
7b: R = *n*-C_5H_{11}

two kinds of methyl protons of the 3-hexyne moiety. In the ^{13}C{^{1}H} NMR spectrum, the quaternary carbons of the oxatantalacyclopentene fragment were observed at δ 100.0 (C_γ), 182.2 (C_β), and 223.9 (C_α).[21] With the exception of the oxatantalacyclopentene fragment, the exact structure of **7a** is still unclear, because the coordination of the other ligands, such as the number of chloride atoms and pyridines, cannot be identified by ^{1}H and ^{13}C{^{1}H} NMR spectroscopies. The most plausible pathway to **7a** from **2a** is that one of the labile pyridine ligands of **2a** is replaced by acetone. However, no signals due to a free pyridine was observed by ^{1}H NMR. The variable-temperature ^{1}H NMR spectrum (−50 to −10 °C) showed three broad singlet peaks (δ 6.54, 6.85, 8.68) assigned to the pyridines. At higher temperatures, we could not observe any signals under various experimental conditions. We suppose that the labile coordinated pyridine ligand dissociates from the tantalum center and recoordinates rapidly on the NMR time scale, and thus no free pyridine signals were observed by NMR spectroscopy. We cannot rule out another possible pathway to **7a**, which is formed by the exchange of a chloride anion of **2a** for acetone. The oxatantalacyclopentene fragment of **7b** derived from **2b** and acetone was also characterized by ^{1}H and ^{13}C{^{1}H} NMR. The ^{13}C signals of quaternary carbon atoms, which construct the oxatantalacyclopentene, appeared at δ 100.1 (C_γ), 181.6 (C_β), and 223.9 (Cα). Hydrolysis of **7b** using aqueous NaOH gave the corresponding allylic alcohol **8** in 83% yield (eq 3). This result also suggests the proposed oxatantalacyclopentene structures.



(3)

Conclusions

We have isolated and characterized new tantalum-η^2-alkyne complexes possessing a DME ligand. These were prepared by a reaction of low-valent tantalum, which was derived by reduction of tantalum pentachloride with zinc, and the corresponding alkynes. The coordinated DME ligand was labile and easily substituted by pyridine, bipyridine, and TMEDA to afford the corresponding amine complexes. The bis(pyridine) complexes were intermediates in the formation of allylic alcohols from alkynes and aldehydes using low-valent tantalum reagent systems. The coordination of pyridine to the tantalum center of the η^2-alkyne complex was required to afford the corresponding allylic alcohol upon treatment with aldehydes and is consistent with our previous results. In addition, the oxatantalacyclopentene fragment derived from the insertion of a carbonyl group of acetone into the tantalacyclopropene was observed in solution by ^{1}H and ^{13}C{^{1}H} NMR spectroscopies.

Experimental Section

All manipulations involving air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under argon. 1,2-Dimethoxyethane (DME), THF, and toluene were purchased from Wako Pure Chemical Industries, Ltd. and stored on 4 Å molecular sieves under argon. Tantalum pentachloride was purchased from Nacalai Tesque, Inc. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-LA400 spectrometer. All ^{1}H NMR chemical shifts were reported in ppm relative to protio impurity resonance as follows: $CDCl_3$, singlet at 7.26 ppm; C_6D_6, singlet at 7.20 ppm; CD_2Cl_2, triplet at 5.35 ppm; $C_6D_5CD_3$, quintet at 2.09 ppm. Other spectra were recorded using the following instruments: IR, Nicolet PROTÉGÉ 460T; UV/vis spectra, Jasco V-570. Elemental analyses were performed at RIKEN. Elemental analysis of **1d**, **2c**, and **2d** led to low observed values for carbon under various analytical conditions. Similar results also have been reported for group 5 complexes.[35−37] All melting points were measured in sealed tubes and were not corrected.

Preparation of DME Complexes 1. A typical procedure is described for the preparation of **1a**. Toluene (16 mL) was added to $TaCl_5$ (1.2 g, 3.3 mmol) in an 80 mL Schlenk tube, and then DME (16 mL) was slowly added to the resulting yellow suspension. Zn powder (0.32 g, 4.9 mmol) was added to the mixture in one portion at room temperature. After stirring the mixture at room temperature for 40 min, the low-valent tantalum was prepared in quantitative yield. 3-Hexyne (0.37 mL, 3.3 mmol) was added to the suspension and stirred at 50 °C for 2 h. All volatiles were removed in vacuo, and the resulting orange powder was extracted with toluene (50 mL). The extract was placed in a −20 °C freezer. Upon standing overnight, orange crystals were deposited. Removal of the supernatant by a syringe afforded 0.98 g (2.1 mmol, 65%) of **1a** in 65% yield. Mp: 129−130 °C (dec). ^{1}H NMR ($C_6D_5CD_3$): δ 1.37 (t, J = 7.5 Hz, 6H, ≡CCH$_2$C*H*$_3$), 3.10−3.17(m, 4H, −OC*H*$_2$C*H*$_2$O−), 3.13 (s, 3H, −OC*H*$_3$), 3.60 (q, J = 7.5 Hz, 4H, ≡CC*H*$_2$CH$_3$), 3.59 (s, 3H, −OC*H*$_3$). ^{13}C{^{1}H} NMR plus DEPT (CD_2Cl_2): δ 13.2 (≡CCH$_2$*C*H$_3$), 33.3 (≡C*C*H$_2$CH$_3$), 62.1 (−O*C*H$_3$), 68.9 (−O*C*H$_3$), 70.6 (−O*C*H$_2$CH$_3$O−), 76.4 (−OCH$_2$*C*H$_2$O−), 256.0 (≡*C*CH$_2$CH$_3$). IR (Nujol/CsI): 1622 (ν C≡C), 312 (ν Ta−Cl) cm^{-1}. Anal. Calcd for $C_{10}H_{20}Cl_3O_2Ta$: C, 26.14; H, 4.39. Found: C, 25.92; H, 4.47.

$TaCl_3$(6-dodecyne)(dme) (1b): 75% yield, recrystallized from 1:1 toluene/hexane. Mp: 70−72 °C (dec). ^{1}H NMR (C_6D_6): δ 0.95 (t, J = 6.3 Hz, 6H, ≡C(CH$_2$)$_4$C*H*$_3$), 1.40−1.43 (m, 8H, ≡C(CH$_2$)$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.94−2.01 (m, 4H, ≡CCH$_2$-C*H*$_2$(CH$_2$)$_2$CH$_3$), 3.13−3.21 (m, 4H, ≡CC*H*$_2$(CH$_2$)$_3$CH$_3$), 3.22 (s, 3H, −OC*H*$_3$), 3.67 (s, 3H, −OC*H*$_3$), 3.78 (t, J = 7.6 Hz, 4H, −OC*H*$_2$C*H*$_2$O−). ^{13}C{1H} NMR plus DEPT (C_6D_6): δ 14.3 (≡C(CH$_2$)$_4$*C*H$_3$), 22.9 (≡C(CH$_2$)$_3$*C*H$_2$CH$_3$), 29.0 (≡C(CH$_2$)$_2$*C*H$_2$-CH$_2$CH$_3$), 32.7 (≡CCH$_2$*C*H$_2$(CH$_2$)$_2$CH$_3$), 40.7 (≡C*C*H$_2$(CH$_2$)$_3$-CH$_3$), 62.3 (−O*C*H$_3$), 68.0 (−O*C*H$_3$), 70.4 (−O*C*H$_2$CH$_2$O−), 75.9 (OCH$_2$*C*H$_2$O), 253.6 (≡*C*(CH$_2$)$_4$CH$_3$). IR (Nujol/CsI): 1686 (ν C≡C), 325 (ν Ta−Cl) cm^{-1}. Anal. Calcd for $C_{16}H_{32}Cl_3O_2Ta$: C, 35.34; H, 5.93. Found: C, 35.26; H, 5.74.

$TaCl_3$(1-phenyl-1-propyne)(dme) (1c): 57% yield, recrystallized from toluene. Mp: 152−156 °C (dec). ^{1}H NMR (C_6D_6): δ 3.05 (s, 3H, ≡CC*H*$_3$), 3.09−3.13 (m, 4H, −OC*H*$_2$C*H*$_2$O−), 3.61 (s, 3H, −OC*H*$_3$), 3.70(s, 3H, −OC*H*$_3$), 7.15−−7.17 (m, 1H, *H*$_{p-Ph}$), 7.35 (t, J = 7.8 Hz, 2H, *H*$_{o-Ph}$), 7.96−7.98 (m, 2H, *H*$_{m-Ph}$). ^{13}C{^{1}H} NMR plus DEPT (C_6D_6): δ 24.6 (≡C*C*H$_3$), 62.6 (−O*C*H$_3$), 69.0 (−O*C*H$_3$), 70.9 (−O*C*H$_2$CH$_2$O−), 76.6 (−OCH$_2$-*C*H$_2$O−), 126.1, 127.7, 128.4, 129.5, 131.3, 140.7 (*C*$_{ipso-Ph}$), 242.0 (≡*C*CH$_3$), 256.4 (≡*C*Ph). IR (Nujol/CsI): 1672 ($\nu_{C\equiv C}$), 310 (ν_{Ta-Cl}) cm^{-1}. Anal. Calcd for $C_{13}H_{18}Cl_3O_2Ta$: C, 31.63; H, 3.68. Found: C, 31.40; H, 3.40.

$TaCl_3$(diphenylacetylene)(dme) (1d): 65% yield, recrystallized from toluene/hexane. Mp: 143−146 °C (dec). ^{1}H NMR (C_6D_6): δ 3.11 (s, 3H, −OC*H*$_3$), 3.11−3.17(m, 4H, −OC*H*$_2$C*H*$_2$-O−), 3.73 (s, 3H, −OC*H*$_3$), 7.01−7.11 (m, 2H, H, *H*$_{p-Ph}$), 7.30 (t, J = 7.8 Hz, 4H, *H*$_{o-Ph}$), 8.07 (t, J = 8.4 Hz, 4H, H, *H*$_{m-Ph}$). ^{13}C NMR (C_6D_6): δ 62.8 (−O*C*H$_3$), 68.5 (−O*C*H$_3$), 70.8 (−O*C*H$_2$-CH$_2$O−), 76.3 (−OCH$_2$*C*H$_2$O−), 128.8, 129.7, 130.8, 142.6 (*C*$_{ipso-Ph}$), 244.2 (≡*C*Ph). IR (Nujol/CsI): 1699 (ν C≡C), 303 (ν Ta−Cl) cm^{-1}. Anal. Calcd for $C_{18}H_{20}Cl_3O_2Ta$: C, 38.91; H, 3.67. Found: C, 33.47; H, 3.34.

Preparation of Pyridine Complexes 2. A typical procedure is described for the preparation of **2a**. To a solution of **1a** (0.19 g, 0.42 mmol) in toluene (25 mL) was added pyridine (0.068 g, 0.85 mmol). The color of the mixture turned to red. After stirring for 30 min, the red solution was concentrated to 5 mL in vacuo and cooled to −20 °C for 2 days. Complex **2a** was obtained as red crystals (0.094 g, 0.18 mmol) in 42% yield, mp 157−158 °C (dec). ^{1}H NMR plus ^{1}H−^{1}H COSY (C_6D_6): δ 1.41 (t, J = 7.5 Hz, 6H, ≡CCH$_2$C*H*$_3$), 3.73 (q, J = 7.5 Hz, 4H, ≡CC*H*$_2$CH$_3$), 6.29 (t, J = 7.2 Hz, 2H, *H*$_{o-pyridine-A}$), 6.53 (t, J = 6.6 Hz, 2H, *H*$_{o-pyridine-B}$), 6.69 (t, J = 7.6 Hz, 1H, *H*$_{p-pyridine-A}$), 6.83 (t, J = 7.4 Hz, 1H, *H*$_{p-pyridine-B}$), 8.67 (d, J = 5.1 Hz, 2H, *H*$_{m-pyridine-B}$), 9.31 (brs, 2H, *H*$_{m-pyridine-A}$). ^{13}C{^{1}H} NMR plus DEPT (CD_2Cl_2): δ 13.3 (≡CCH$_2$*C*H$_3$), 33.4 (≡C*C*H$_2$CH$_3$), 124.5, 139.2, 151.8, 256.4 (≡*C*CH$_2$CH$_3$). IR (Nujol/CsI): 1640 ($\nu_{C\equiv C}$), 322 (ν_{Ta-Cl}) cm^{-1}. Anal. Calcd for $C_{16}H_{20}Cl_3N_2Ta$: C, 36.42; H, 3.82; N, 5.31. Found: C, 36.12; H, 3.89; N, 5.50.

$TaCl_3$(6-dodecyne)(py)$_2$ (2b): 87% yield, recrystallized from toluene/hexane. Mp: 48−52 °C (dec). ^{1}H NMR plus ^{1}H−^{1}H COSY (C_6D_6): δ 0.93 (t, J = 7.2 Hz, 6H, ≡C(CH$_2$)$_4$C*H*$_3$), 1.35−1.47 (m, 8H, ≡C(CH$_2$)$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.92−2.00 (m, 4H, ≡CCH$_2$C*H*$_2$(CH$_2$)$_2$CH$_3$), 3.80 (t, J = 7.6 Hz, 4H, ≡CC*H*$_2$(CH$_2$)$_3$-CH$_3$), 6.36 (t, J = 6.8 Hz, 2H, *H*$_{o-pyridine-A}$), 6.57 (brs, 2H, *H*$_{o-pyridine-B}$), 6.76 (t, J = 7.7 Hz, 1H, *H*$_{p-pyridine-A}$), 6.88 (brs, 1H, *H*$_{p-pyridine-B}$), 8.74 (d, J = 5.5 Hz, 2H, *H*$_{m-pyridine-B}$), 9.32 (brs, 2H, *H*$_{m-pyridine-A}$). ^{13}C{^{1}H} NMR plus DEPT (C_6D_6): δ 14.3 (≡C(CH$_2$)$_4$*C*H$_3$), 23.0 (≡C(CH$_2$)$_3$*C*H$_2$CH$_3$), 29.1 (≡C(CH$_2$)$_2$*C*H$_2$-CH$_2$CH$_3$), 32.8 (≡CCH$_2$*C*H$_2$(CH$_2$)$_2$CH$_3$), 40.9 (≡C*C*H$_2$(CH$_2$)$_3$-CH$_3$), 124.0, 138.4, 152.7, 253.8(≡*C*(CH$_2$)$_4$CH$_3$). IR (Nujol/CsI): 1634 ($\nu_{C\equiv C}$), 301 (ν_{Ta-Cl}) cm^{-1}. Anal. Calcd for $C_{22}H_{32}Cl_3N_2Ta$: C, 43.19; H, 5.27; N, 4.58. Found: C, 43.07; H, 4.99; N, 4.32.

$TaCl_3$(1-phenyl-1-propyne)(py)$_2$ (2c): 61% yield, recrystallized from CH_2Cl_2/hexane. Mp: 207−208 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 3.49 (s, 3H, ≡CC*H*$_3$), 7.28−7.53 (m, 9H), 7.86−7.96 (m, 2H), 8.59 (d, J = 5.1 Hz, 2H, *H*$_{m-pyridine-B}$), 9.51 (brs, 2H, *H*$_{m-pyridine-A}$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 24.7 (≡C*C*H$_3$), 124.5, 128.1, 130.0, 131.1, 139.3, 141.7 (*C*$_{ipso-Ph}$), 151.9, 243.7 (≡*C*CH$_3$), 256.2 (≡*C*Ph). IR (Nujol/CsI): 1650 ($\nu_{C\equiv C}$), 292 (ν_{Ta-Cl}) cm^{-1}. Anal. Calcd for $C_{19}H_{18}Cl_3N_2Ta$: C, 40.63; H, 3.23; N, 4.99. Found: C, 39.92; H, 3.19; N, 4.96.

$TaCl_3$(diphenylacetylene)(py)$_2$ (2d): 36% yield, recrystallized from CH_2Cl_2/hexane. Mp: 223−226 °C (dec). ^{1}H NMR plus ^{1}H−^{1}H COSY (CD_2Cl_2): δ 7.21−7.24 (m, 2H, *H*$_{o-pyridine-A}$), 7.25−7.29 (m, 2H, *H*$_{p-Ph}$), 7.41 (t, J = 7.6 Hz, 4H, *H*$_{m-Ph}$), 7.49 (m, 2H, *H*$_{o-pyridine-B}$), 7.59 (d, J = 6.9 Hz, 4H, *H*$_{o-Ph}$), 7.76−7.81 (m, 1H, *H*$_{p-pyridine-A}$), 7.96 (t, J = 7.6 Hz, 1H, *H*$_{p-pyridine-B}$), 8.59 (d, J = 5.1 Hz, 2H, *H*$_{m-pyridine-A}$), 9.20 (brs, 2 H, *H*$_{m-pyridine-B}$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 124.4, 127.9, 128.8, 129.8, 139.1, 142.2 (*C*$_{ipso-Ph}$), 152.1, 244.2(≡*C*Ph). IR (Nujol/CsI): 1650 ($\nu_{C\equiv C}$), 292 (ν_{Ta-Cl}) cm^{-1}. Anal. Calcd for $C_{24}H_{20}Cl_3N_2Ta$: C, 46.22; H, 3.23; N, 4.49. Found: C, 45.37; H, 3.03; N, 4.54.

NMR Experiment of Ligand Exchange Reaction of 1a. Pyridine (3.2 μL, 0.040 mmol) was added to a solution of **1a** (9.0 mg, 0.020 mmol) in C_6D_6 (0.70 mL) containing 1,2-dichloroethane (3.0 μL) as an internal standard in a NMR tube. The NMR spectrum of the sample was measured after standing at room temperature for 30 min. Product ratios were determined by integration of peak area of the ^{1}H NMR spectrum. The peak area of the product was given as follows:

(36) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.
(37) Murphy, V. J.; Turner, H. *Organometallics* **1997**, *16*, 2495.

400 for of **1a** (4H, $TaCl_3$(3-hexyne)(MeOCH_2CH_2OMe)); 403 for 1,2-dimethoxyethane (4H, MeOCH_2CH_2OMe), and 856 for 1,2-dichloroethane (4H, ClCH_2CH_2Cl). From these values, the yields of **2a** and 1,2-dimethoxyethane were calculated to both be in 91% yield based on the internal standard.

$TaCl_3$(3-hexyne)(bipy) (3). This complex was prepared in a similar manner described for **2a**: 49% yield, recrystallized from CH_2Cl_2. Mp: 234−236 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.42 (t, J = 7.5 Hz, 6H, ≡CCH$_2$CH_3), 3.72 (q, J = 7.5 Hz, 4H, ≡CCH_2CH$_3$), 7.62−7.66 (m. 1H), 7.73−7.76 (m, 1H), 8.17−8.24 (m, 2H), 8.31−8.35 (m, 2H), 8.74−8.76 (m, 1H), 9.87−9.89 (m, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 13.4 (≡CCH$_2$CH_3), 34.2 (≡CCH_2CH$_3$), 122.8, 123.0, 126.4, 126.6, 139.9, 140.8, 149.4, 151.9, 152.5, 153.3, 260.7 (≡CCH$_2$CH$_3$). IR (Nujol/CsI): 318 (ν_{Ta-Cl}) cm^{-1}. Anal. Calcd for $C_{16}H_{18}Cl_3N_2Ta$: C, 36.56; H, 3.45; N, 5.33. Found: C, 36.38; H, 3.27; N, 5.25.

$TaCl_3$(3-hexyne)(tmeda) (4). This complex was prepared in a similar manner described for **2a**: 61% yield, recrystallized from toluene/hexane. Mp: 100−102 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.41 (t, J = 7.5 Hz, 6H, CH$_2$CH_3), 2.09 (m, 4H, CH_2), 2.36 (s, 6H, N(CH_3)$_2$), 2.74 (s, 6H, N(CH_3)$_2$), 3.68 (q, J = 7.5 Hz, 4H, CH_2CH$_3$). ^{13}C{^{1}H} NMR plus DEPT (C_6D_6): δ 14.0 (≡CCH$_2$CH_3), 34.2 (≡CCH$_2$CH_3), 50.8 (N(CH_3)$_2$), 53.7 (N(CH_3)$_2$), 57.3 (NCH_2CH$_2$N), 61.0 (NCH$_2$CH_2N), 256.1 (≡CCH$_2$CH$_3$). IR (Nujol/CsI): 1675 ($\nu_{C\equiv C}$), 316 (ν_{Ta-Cl}) cm^{-1}. Anal. Calcd for $C_{12}H_{26}Cl_3N_2Ta$: C, 29.68; H, 5.40; N, 5.77. Found: C, 29.55; H, 5.46; N, 5.68.

Crystallographic Data Collections and Structure Determination of 1a, 1c, 2a, and 4. Data Collection. A suitable crystal of each compound was mounted in a glass capillary under an argon atmosphere. Data for complexes **1a**, **1c**, and **2a** were collected by a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation and a 12 kW rotating anode generator. The incident beam collimator was 1.0 mm, and the crystal-to-detector distance was 285 mm. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections, corresponded to the cells with dimensions listed in Table 2, where details of the data collection are summarized. The weak reflections (I < 10σ(I)) were rescanned (maximum of 2 rescans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. Three standard reflections were chosen and monitored every 150 reflections. For complex **4**, measurement was made on a Rigaku RAIS-IV imaging plate diffractometer with graphite-monochromated Mo Kα (λ = 0.71069 Å). The incident beam collimator was 0.5 mm, and the crystal-to-detector distance was 100.02 mm with the detector at the zero swing position. Indexing was performed from four oscillations which were exposed for 4.0 min. The readout was obtained in the 0.100 mm pixel mode. A total of 45 plates of 4.00° oscillation images were collected, each being exposed for 4.0 min. Cell constants are listed in Table 2.

Data Reduction. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. The decays of intensities of three representative reflections were −6.57% for **1a**, −5.10% for **1c**, and −12.45% for **2a**, and thus linear correction factors were applied to the decay of these observed data. Complex **4** showed no decay.

Structure Determination and Refinement. All calculations were performed using a teXsan crystallographic software package,[38] and illustrations were drawn with Ortep-3 for Windows.[39] Crystallographic calculations were performed on an SGI O_2 workstation at Venture Business Laboratory, Graduate School of Okayama University. In the subsequent refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as R1 = $\sum||F_o| - |F_c||/\sum|F_o|$ and wR2 = $[\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$, respectively. Atomic positional parameters for the non-hydrogen atoms of all complexes are given in the Supporting Information.

Reaction of Tantalum-Alkyne Complexes with 3-Phenylpropanal. A typical procedure is described for the reaction of **2a** with 3-phenylpropanal. To a solution of **2a** (0.10 g, 0.20 mmol) in toluene (8 mL) was added 3-phenylpropanal (0.027 mL, 0.20 mmol) and stirred at 25 °C for 1.5 h. After addition of aqueous NaOH (15 wt %), the mixture was stirred for 30 min. The reaction mixture was passed through a Hyflo-Super Cel, and organic products were extracted with ether (10 mL × 3). The combined extracts were dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by preparative TLC on silica gel (benzene/ethyl acetate, 30:1) gave (*E*)-4-ethyl-1-phenyl-4-hepten-3-ol (0.033 g, 0.15 mmol) in 77% yield. Bp: 95 °C (0.9 Torr). ^{1}H NMR ($CDCl_3$): δ 0.99 (t, J = 7.5 Hz, 3H), 1.01 (t, J = 7.6 Hz, 3H), 1.38 (brs, 1H), 1.87 (q, J = 7.5 Hz, 2H), 2.02−2.13 (m, 4H), 2.58 −2.77(m, 2H), 4.03−4.07 (m, 1H), 5.37 (t, J = 7.0 Hz, 1H), 7.18−7.30 (m, 5H). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 14.9, 15.2, 20.6, 21.2, 32.8, 76.8, 126.2, 128.8, 129.0, 129.1, 142.7, 143.0. IR (Nujol/CsI): 3350, 3050, 2960, 2870, 1605, 1495, 1450, 1050, 860, 750, 695 cm^{-1}.

NMR Characterization of Oxatantalacyclopentene Complexes 7a and 7b. 7a: Acetone (4.6 μL, 0.062 mmol) was added to a solution of **2a** (33.0 mg, 0.062 mmol) in $C_6D_5CD_3$ (0.70 mL) at room temperature in a NMR tube. During the reaction, the color of the mixture gradually turned from reddish orange to yellow. The NMR spectrum of the sample was measured after standing at room temperature for 30 min. ^{1}H NMR ($C_6D_6CD_3$, 263 K): δ 0.82 (t, J = 7.6 Hz, 3H), 1.13 (s, 6H), 1.48 (t, J = 7.6 Hz, 3H), 3.28 (q, J = 7.6 Hz, 2 H), 6.54 (brs, 4H), 6.85 (brs, 2H), 8.68 (brs, 4H). ^{13}C{^{1}H} NMR plus DEPT ($C_6D_5CD_3$, 263 K): δ 14.1, 165.5, 22.5, 27.2, 35.7, 100.0, 124.0, 137.4, 149.5, 182.2. **7b**: Acetone (2.6 μL, 0.035 mmol) was added to a solution of **2b** (21.0 mg, 0.035 mmol) in C_6D_5-CD_3 (0.70 mL) at room temperature in a NMR tube. During the reaction, the color of the mixture gradually turned from reddish orange to yellow. The NMR spectrum of the sample was measured after standing at room temperature for 30 min. ^{1}H NMR ($C_6D_5CD_3$, 263 K): δ 0.86 (t, J = 6.9 Hz, 3H), 0.99 (t, J = 6.7 Hz, 3H), 1.00−1.27 (m, 6H), 1.39 (s, 6H), 1.49 (brs, 4H), 1.81 (t, J = 8.1 Hz, 2H), 2.02 (brs, 2H), 3.45 (t, J = 7.7 Hz, 2H), 6.57 (brs, 4H), 6.86 (brs, 2H), 8.66 (brs, 4H). ^{13}C{^{1}H} NMR plus DEPT ($C_6D_5CD_3$, 263 K): δ 14.3, 14.6, 22.7, 23.1, 27.5, 29.6, 30.1, 30.5, 33.0, 33.2, 43.0, 100.1, 124.1, 137.4, 149.4, 181.6, 223.9.

Hydrolysis of 7b. Complex **7b** was generated in situ by the addition of acetone (13 μL, 0.18 mmol) to **2b** (0.108 g, 0.18 mmol) in toluene (5 mL). The reaction mixture was stirred at 25 °C for 2.5 h. After 15% aqueous NaOH was added and stirred for 30 min, the mixture was passed through a Hyflo-Super Cel and organic products were extracted with ether (10 mL × 3). The combined extracts were dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by preparative TLC on silica gel (hexane/ethyl acetate, 3:1) gave **8** (0.033 g, 0.15 mmol) in 83% yield. ^{1}H NMR ($CDCl_3$): δ 0.94 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H), 1.04 (brs, 1H), 1.32 (s, 6H), 1.33−1.37 (m, 8H), 1.39−1.47 (m, 2H), 2.08−2.18 (m, 4H), 5.59 (t, J = 7.1 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.26, 14.30, 22.9, 23.0, 28.3, 28.4, 30.0, 30.1, 30.9, 32.1, 33.0, 73.3, 123.3, 146.5.

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(38) *teXsan*, Crystal Structure Analysis Package; Molecular Structure Corporation, 1985 and 1992.
(39) Ortep-3 for Windows. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Supporting Information Available: Structural drawings of **1a**, **1c**, **2a**, and **4** and tables of X-ray crystallographic data, atomic coordinates, anisotropic thermal parameters, and a complete list of bond distances and angles are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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