Organometallics **1990**, *9*, 3028-3030

Reactions of Thexylborane with (Phosphine)rhodium Hydride, Alkyl, and Allyl Complexes†

R. Thomas Baker,* Derick W. Ovenall, and Richard L. Harlow

Central Research and Development Department, E. I. du Pont de Nemours and Co.,
Experimental Station, Wilmington, Delaware 19880-0328

Stephen A. Westcott, Nicholas J. Taylor, and Todd B. Marder*

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received September 13, 1990

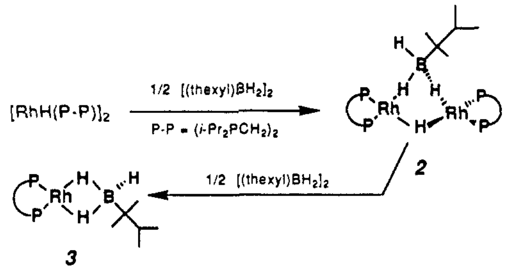
Summary: Differences in the reactivity of saturated and unsaturated chelating bis(phosphine)rhodium complexes with thexylborane are described. Reaction of $[(Pr^i_2PCH_2)_2]Rh(\eta\text{-}2\text{-Me-allyl})$ with thexylborane leads to B–C bond formation at both allyl termini.

We recently reported[1] the preparation and molecular structures of Ir–BR_2, –BRH, and –CH_2BR_2 complexes via oxidative addition of B–H bonds and are currently investigating their reactivity with unsaturated organic substrates. Identification of various modes of reactivity of transition-metal hydrides and alkyls with organoborane reagents is particularly important, as these species are all present in solution during rhodium-catalyzed alkene hydroborations.[2] We now describe the reactions of thexylborane ($[BH(CMe_2CHMe_2)(\mu\text{-}H)]_2$) with chelating bis(phosphine)rhodium hydride, alkyl, and allyl complexes.

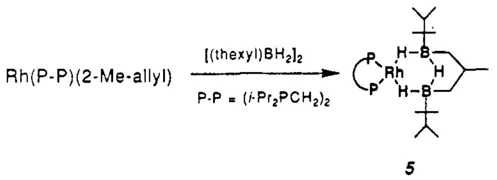
The saturated rhodium hydride $(DMPE)_2RhH$[3] (DMPE = $(Me_2PCH_2)_2$) reacts with 0.5 equiv of thexylborane[4] via hydride transfer to give yellow $[(DMPE)_2Rh]^+[BH_3(thexyl)]^-$ (**1**), characterized by comparison of multinuclear NMR spectra with those of $[(DMPE)_2Rh]Cl$[5] and $Li[BH_3(thexyl)]$.[6]

In contrast, the unsaturated rhodium hydride dimer[7] $[(DiPPE)Rh(\mu\text{-}H)]_2$ (DiPPE = $[Pr^i_2PCH_2]_2$) reacts with 0.5 equiv of thexylborane to give red crystals of the dinuclear complex $[(DiPPE)Rh]_2(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}H_2BH(thexyl)]$ (**2**). Further addition of thexylborane affords orange crystals of mononuclear $(DiPPE)Rh[\eta^2\text{-}H_2BH(thexyl)]$ (**3**). Complexes **2** and **3** were characterized by high-resolution MS, IR, and multinuclear NMR spectroscopy[8] and, for **2**,

Scheme I



Scheme II



by a single-crystal X-ray diffraction study. The molecular structure[9] of **2** (Figure 1A,B) consists of two distorted 16e square-planar Rh(I) centers bridged by hydride and thexylborohydride ligands. The two square planes are twisted with respect to one another (dihedral angle 54.8°) to accommodate the disparate bridges. Similar effects have been observed in two related structures with bridging $(BH_4)^-$ ligands.[10] As expected, **2** is fluxional in solution. The inequivalent P's of the DiPPE ligands, which at −60 °C constitute the $A_2A'_2$ portion of a complicated 10-spin system, are averaged at 25 °C, giving rise to one doublet ^{31}P NMR resonance (J_{PRh} = 170 Hz). In the ^1H NMR spectrum of **2**, the inequivalent Rh–H–B bridges and the terminal B–H of the thexylborohydride ligand undergo rapid exchange; a single broad resonance at δ −4.0 is ob-

---

† Contribution No. 5658.

(1) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.*, in press.

(2) Wilcynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955; **1982**, *21*, 506. Hewes, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 5757. Mannig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878. Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 449. Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 6201. Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 6917. Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 2280. Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178; *Tetrahedron Lett.* **1989**, *30*, 395, 5857, 5861. Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426. Sato, M.; Nomoto, Y.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1989**, *30*, 3789. Sato, M.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1990**, *31*, 231.

(3) Zargarian, D.; Chow, P.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 540.

(4) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988; p 423.

(5) Chatt, J.; Butter, S. A. *Chem. Commun.* **1967**, 501.

(6) Brown, H. C.; Singaram, B.; Mathew, P. C. *J. Org. Chem.* **1981**, *46*, 4541.

(7) Fryzuk, M. D.; Einstein, F. W. B.; Jones, T. *Organometallics* **1984**, *3*, 185.

(8) Selected NMR spectral data in toluene-d_8 at 25 °C are as follows. **2**: $^{31}P\{^1H\}$ 100.8 ppm (br d, J_{PRh} = 170 Hz), at −40 °C, 104.2 (d d, J_{PRh} = 178, $^2J_{PP}$ = 26 Hz), 97.0 ppm (d d, J_{PRh} = 169 Hz); $^{11}B\{^1H\}$ 35.9 ppm (br): ^1H δ −3.70 (br, 2 H, RhHB), −9.63 (tr quint, J_{HRh} = $^2J_{HP}$ = 20 Hz, 1 H, RhHRh). **3**: $^{31}P\{^1H\}$ 112.9 ppm (d, J_{PRh} = 163 Hz); $^{11}B\{^1H\}$ 1.7 ppm (br): ^1H δ −1.53 (br, 2 H, RhHB); $^1H\{^{11}B\}$ δ −1.53 (d tr, J_{HRh} = 23, $^2J_{HP}$ = 15 Hz). **4**: ^{11}B −15.5 ppm (tr, J_{BH} = 66 Hz). **5**: $^{31}P\{^1H\}$ 102.2 ppm (d, J_{PRh} = 180 Hz); $^{11}B\{^1H\}$ 5.4 ppm (br); ^1H δ 2.67 (mult, 1 H, –C*H*Me–), 1.33 (d, $^3J_{HH}$ = 6 Hz, 3 H, –CH*Me*–), −1.34 (br, 1 H, BHB), −5.98 (br, 2 H, RhHB); $^1H\{^{11}B\}$ δ −5.98 (d tr, J_{HRh} = 20, $^2J_{HP}$ = 13 Hz).

(9) Crystal data for **2** (from THF–hexane): $C_{34}H_{81}BP_4Rh_2$, fw 830.55, monoclinic, space group $P2_1/_n$, a = 19.237 (6) Å, b = 12.067 (2) Å, c = 19.496 (4) Å, β = 109.67 (1)°, V = 4261.6 Å^3, Z = 4, ρ(calcd) = 1.294 g cm^{-3}; T = 203 K. Anisotropic refinement of all non-hydrogen atoms (H1, H1′, H1″, H2 isotropic, remaining H's fixed; 386 variables) by use of 7604 reflections with $I > 3\sigma(I)$, from 10 504 unique data collected, gave R = 0.027, R_w = 0.028. Full details are provided in the supplementary material.

(10) $[(\eta\text{-}C_5Me_5)IrH]_2(\mu\text{-}H)(\mu\text{-}H_2BH_2)$: Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508. $[Mn(CO)_3]_2(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}H)(\mu\text{-}H_2BH_2)$: Carreno, R.; Ruiz, M. A.; Jeannin, Y.; Philoche-Levisalles, M. *J. Chem. Soc., Chem. Commun.* **1990**, 15.

0276-7333/90/2309-3028$02.50/0

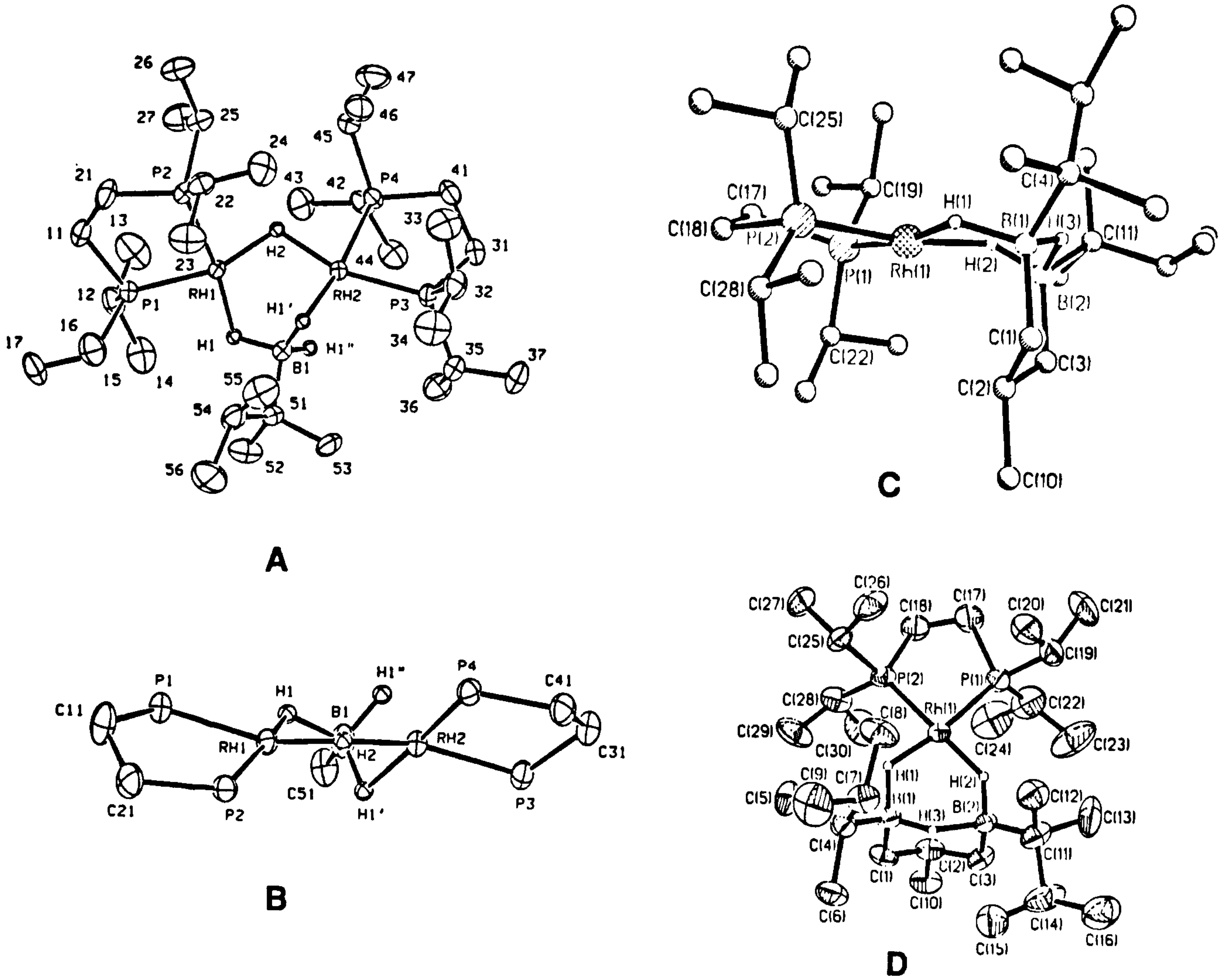


Figure 1. (A) Molecular structure of [(DiPPE)Rh]$_2$(μ-H)(μ-BH$_3$(thexyl)) (2). (B) Detail of the bridges in 2. (C, D) Molecular structure of (DiPPE)Rh(DIBOR) (5; two views). In views C and D, hydrogen atoms (except those on B or Rh) are omitted for clarity.

served, even at −100 °C. A slower exchange of the thexylborohydride H's with the Rh–H–Rh bridge was demonstrated by magnetization transfer experiments. At 25 °C, the Rh–H–Rh bridge is observed as a triplet of quintets at δ −9.63 (J_{HRh} = $^2J_{HP}$ = 20 Hz).

The ^{1}H NMR spectrum of 3 contains a broad resonance at δ −1.53, which gives rise to a doublet of triplets upon ^{11}B decoupling (J_{HRh} = 23 Hz, $^2J_{HP}$ = 15 Hz) and is also assigned to rapidly exchanging terminal and bridging H's of the η^2-thexylborohydride ligand. Assignment of the bidentate coordination mode (vs tridentate) of the thexylborohydride ligand is based on the observation of a weak terminal B–H stretch at 2270 cm^{-1} in the IR spectrum of 3 (vs 1825 cm^{-1} for Rh–H–B stretch).

The methylrhodium complex (DMPE)$_2$RhMe[3] reacts with thexylborane to form initially yellow [(DMPE)$_2$Rh][BH$_2$Me(thexyl)] (4), which slowly converts to (DMPE)$_2$RhH, and presumably [BMe(thexyl)(μ-H)]$_2$.[11]

The unsaturated allylrhodium complex (DiPPE)Rh(η-2-Me-allyl)[12] reacts with 1 equiv of thexylborane dimer to form two B–C bonds, yielding (DiPPE)Rh(DIBOR) (5, DIBOR = 1,5-(μ-hydrido)-1,5-dithexyl-3-methyl-1,5-diborapentane). The molecular structure[13] of 5 (Figure 1C,D) consists of a 16e square-planar Rh(I) center coordinated to the [BH(thexyl)CH$_2$CHMeCH$_2$BH(thexyl)](μ-H) moiety through two Rh–H–B bridges. The latter give rise to a broad ^{1}H NMR resonance at δ −5.98 (doublet of triplets with ^{11}B decoupling, J_{HRh} = 20 Hz, $^2J_{HP}$ = 13 Hz). A broad B–H–B resonance is observed at δ −1.34. The formation of 5 involves two processes, namely hydroboration of the allyl ligand and insertion of thexylborane into a Rh–C bond. As a result, both ends of the allyl group are derivatized in a single reaction. The details of this process are being investigated with use of the hindered dialkylborane 9-borabicyclo[3.3.1]nonane (9-BBN).

The reactions described above demonstrate insertion of B–H bonds into Rh–H and Rh–C bonds and abstraction of hydride and methyl ligands from Rh by thexylborane. In addition, reaction of thexylborane with a (π-allyl)rhodium complex leads to B–C bond formation at both allyl termini. The reactivity of complexes 2, 3, and 5 with

---

(11) The ^{11}B NMR chemical shift of the purported [BMe(thexyl)(μ-H)]$_2$ (27.3 ppm) is typical of H-bridged dimeric organoboranes. See: Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978.

(12) Fryzuk, M. D. *Inorg. Chem.* **1982**, *21*, 2134.

(13) Crystal data for 5 (from hexane): C$_{30}$H$_{69}$B$_2$P$_2$Rh, fw 616.27, orthorhombic, space group $P2_12_12_1$, a = 10.695 (3) Å, b = 17.994 (4) Å, c = 18.736 (5) Å, V = 3606 (2) Å^3, Z = 4, ρ(calcd) = 1.135 g cm^{-3}, T = 295 K. The bridging hydrogen atoms (H1, H2, H3) were located but not refined. Anisotropic refinement of all non-hydrogen atoms by use of 2768 reflections with $I > 3\sigma(I)$, from 3555 unique data collected, gave R = 0.051, R_w = 0.054. Full details are provided in the supplementary material.

unsaturated organic substrates is under investigation.

Acknowledgment. We thank T. J. Onley, E. A. Conaway, and L. F. Lardear for expert technical assistance. T.B.M. acknowledges support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Natural Sciences and Engineering Research Council of Canada.

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†

Kazuhiko Takai,* Jiro Miyai, Yasutaka Kataoka, and Kiitiro Utimoto*

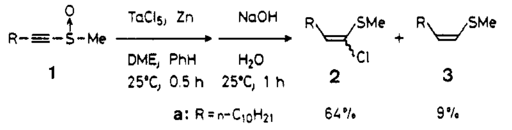
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Received September 13, 1990

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.

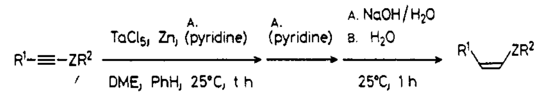
Formation of tantalum–alkyne complexes from alkynyl sulfides[2] proceeds faster than that of tantalum–dialkylacetylene complexes.[1g] Alkenyl sulfides were produced after alkaline workup.[3] Pretreatment of low-valent tantalum with pyridine before the addition of alkynes prevented the formation of 1-chloro-1-alkenyl 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 **2** **3** (1)

a: R = n-$C_{10}H_{21}$ 64% 9%

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



1

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

---

† 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.

[4] Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 1287.

[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.

0276-7333/90/2309-3030$02.50/0