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Synthesis and Characterization of Trihaloniobium Alkyne Complexes

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Neutral, monomeric trihaloniobium alkyne complexes of the general formula $L_nX_3Nb(RC{\equiv}CR')$ (X = Cl, Br L = dimethoxyethane (DME, *n* = 1); X = Cl, L = tetrahydrofuran (THF, *n* = 2)) are conveniently prepared from the reaction of NbX_3(DME) with alkynes. An X-ray crystal structure of $(THF)_2Cl_3Nb(PhC{\equiv}CSi(t\text{-}Bu)Me_2)$ was obtained and indicates that the alkyne unit is bound to niobium in a highly symmetric fashion with identical niobium–carbon distances (2.067 (2) Å). The synthesis of $NbBr_3$(DME) is reported.

Introduction

Recently we have described a synthesis of 2,3-disubstituted 1-naphthols that relies on the generation of niobium alkyne complexes of the type $(THF)_2Cl_3Nb(RC{\equiv}CR')$.[1] Beyond applications in organic synthesis,[1,2] there has been steady interest in the general organometallic chemistry of niobium and tantalum alkyne complexes.[3] In the majority of these cases one or more aryloxide or cyclopentadienyl group is ligated to the metal.[3] Often these species are derived from the two-electron reduction of d^0 precursors that already bear these ancillary ligands. An intermediate d^2 species is then trapped by having an alkyne present (generally an excess is employed). An alternative and potentially more versatile approach to the synthesis of such compounds would involve beginning with a readily available source of niobium alkyne complexes that contain easily replaced ligands. Herein we report on the synthesis and characterization of a general and synthetically useful class of niobium alkyne complexes, $L_nX_3Nb(RC{\equiv}CR')$ (X = Cl, Br, L = dimethoxyethane (DME, *n* = 1); X = Cl, L = tetrahydrofuran (THF, *n* = 2)).

Table I. Niobium Alkyne Complexes $(DME)X_3Nb(RC{\equiv}CR')$

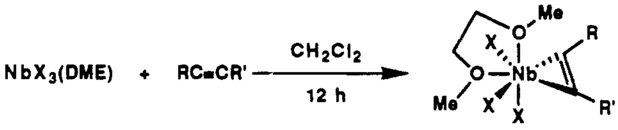
compd	X	R	R′
3a	Cl	Ph	Ph
3b	Cl	Ph	Et
3c	Cl	Et	Et
3d	Cl	Me	Me
3e	Cl	Me_3Si	H
3f	Cl	Me_3Si	*n*-Pr
3g	Br	Ph	$(t\text{-}Bu)Me_2Si$
3h	Br	Et	Et
4a	Cl	Me	Me
4b	Cl	Ph	Et
4c	Cl	*t*-Bu	Me
4d	Cl	Ph	$(t\text{-}Bu)Me_2Si$

Results and Discussion

The preparation and synthetic organic applications of the new niobium(III) reagent $NbCl_3$(DME) (**1**) have been recently reported.[4] The ease with which this reagent is prepared makes it a particularly attractive starting material for a variety of organic and inorganic applications.[5] The bromide analogue $NbBr_3$(DME) (**2**) is prepared in a similar manner from niobium pentabromide and 2 equiv of tributyltin hydride in 88% yield as illustrated in eq 1.

$$NbBr_5 + 2\,Bu_3SnH \xrightarrow[-78\,°C]{DME} NbBr_3(DME) + 2\,Bu_3SnBr + H_2 \qquad (1)$$

Reaction of **1** or **2** with an internal alkyne in dichloromethane for 12 h provides good yields of the niobium alkyne complexes $(DME)X_3Nb(RC{\equiv}CR')$ (**3**), as shown in eq 2 (see Table I). The ^1H and ^{13}C NMR spectra of



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compounds derived from symmetrical alkynes indicate a structure in which both alkyne substituents are equivalent. This is consistent with the structure shown in eq 2 and also in accord with an X-ray structure of a related bis(tetrahydrofuran) complex (vide infra). In the ^{13}C NMR spectra of these derivatives, the acetylenic carbons fall within the range generally ascribed to complexes containing alkyne ligands that act as four-electron donors (i.e. 180–225 ppm).[6]

Reaction of **1** with (trimethylsilyl)acetylene in dichloromethane provides the corresponding terminal alkyne complex. However, less hindered terminal alkynes such

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(1) Hartung, J. B., Jr.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 5468.

(2) Williams, A. C.; Sheffels, P.; Sheehan, D.; Livinghouse, T. *Organometallics* **1989**, *8*, 1566.

(3) This list is meant to be representative and not exhaustive. (a) Vrtis, R. N.; Rao, C. P.; Bott, S. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 7564. (b) Bartlett, R. A.; Power, P. P.; Shoner, S. C. *Ibid.* **1988**, *110*, 1966. (c) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067. (d) McGeary, M. J.; Gamble, A. S.; Templeton, J. L. *Ibid.* **1988**, *7*, 271 and references therein. (e) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525. (f) Antinolo, A.; Gómez-Sal, P.; Martínez de Ilarduya, J.; Otero, A.; Royo, P. *J. Chem. Soc., Dalton Trans* **1987**, 975. (g) Alt, H. G.; Engelhardt, H. E. *Z. Naturforsch., B. Chem. Sci.* **1987**, *42*, 711. (h) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668. (i) Arnold, J.; Shina, D. N.; Tilly, T. D. *Organometallics* **1986**, *5*, 2037. (j) Curtis, M. D.; Real, J. *Ibid.* **1985**, *4*, 940. (k) Belmonte, P. A.; Cloke, F. G. N.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 2365. (l) Cotton, F. A.; Roth, W. J. *Inorg. Chim. Acta* **1984**, *85*, 17. (m) Hey, E.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *514*, 25. (n) Hey, E.; Weller, F.; Dehnicke, K. *Naturwissenschaften* **1983**, *70*, 41. (o) Serrano, R.; Royo, P. *J. Organomet. Chem.* **1983**, *247*, 33. (p) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1981**, *20*, 1285. (q) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Ibid.* **1981**, *20*, 387. (r) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (s) Sala-Pala, J.; Amaudrut, J.; Guerchais, J. E.; Mercier, R.; Douglade, J.; Theobald, J. G. *J. Organomet. Chem.* **1981**, *204*, 347. (t) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354. (u) Cotton, F. A.; Hall, W. T. *Ibid.* **1980**, *19*, 2352. (v) Fredericks, S.; Thomas, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 350. (w) Labinger, J. A.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 1596. (x) Labinger, J. A.; Schwartz, J.; Townsend, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4009. (y) Nesmeyanov, A. N.; Gusev, A. I.; Pasynskii, A. A.; Amisimov, K. N.; Kolobova, N. E.; Struchkov, Y. T. *J. Chem. Soc. D* **1969**, 277. (z) Nesmeyanov, A. N.; Gusev, A. I.; Pasynskii, A. A.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Y. T. *J. Chem. Soc. D* **1968**, 1365.

(4) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 6551.

(5) $NbCl_3$(DME) is also commercially available from Aldrich Chemical Co.

(6) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532.

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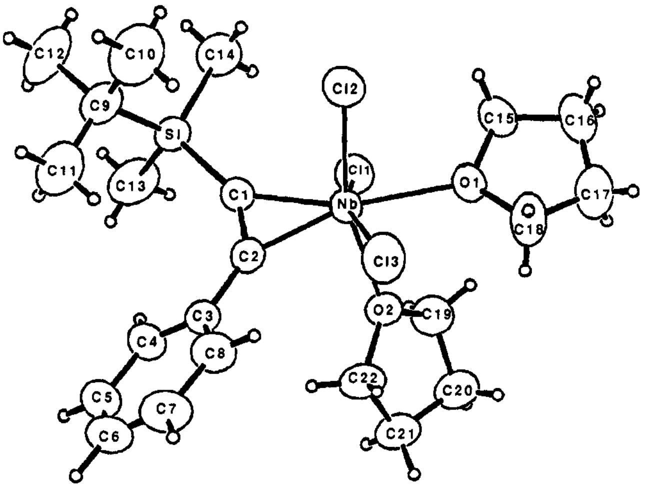
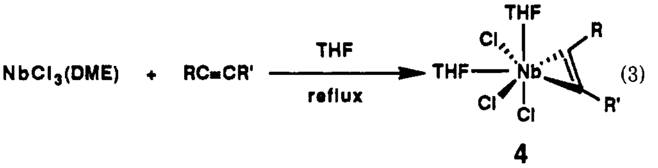


Figure 1. ORTEP drawing of **4d** (50% probability) with numbering scheme.

as 1-hexyne are cyclotrimerized, providing a mixture of 1,3,5- and 1,2,4-trisubstituted benzenes (this reaction is also catalytic in **1**; see Experimental Section).[7] Trialkyltin-substituted alkynes do not give rise to tractable products when reacted with **1**. This may be the result of cleavage of the weak Sn–C_{sp} bond, leading to acetylide complexes. Sterically hindered alkynes such as 2,2,5,5-tetramethyl-3-hexyne or bis(trimethylsilyl)acetylene do not give rise to significant amounts of any new compounds.

The dimethoxyethane-substituted alkyne complexes are partially soluble in solvents such as benzene or toluene. They readily dissolve in dichloromethane but exhibit immediate decomposition in chloroform. Tetrahydrofuran readily solubilizes these alkyne complexes with concomitant substitution of the dimethoxyethane ligand for two tetrahydrofuran ligands (established by ^1H NMR spectroscopy).

A more general route to complexes with the formula $(THF)_2Cl_3Nb(RC{\equiv}CR')$ (**4**) is outlined in eq 3 (see Table I). Good yields of these compounds are obtained only if



(3)

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the reaction mixture is gently refluxed. Similar reactions at room temperature lead to lowered yields, primarily due to difficulties associated with separating the desired alkyne complexes from uncharacterized byproducts.[8]

An X-ray crystal structure of $(THF)_2Cl_3Nb(PhC{\equiv}CSi(t\text{-}Bu)Me_2)$ (**4d**) was obtained and is shown in Figure 1.[17] The alkyne unit is bound to niobium in a highly symmetric fashion with identical niobium–carbon distances and near-identical O(1)–Nb–C angles (see Table II). The alkyne carbon–carbon bond distance of 1.306 (3) Å is slightly shorter than a typical carbon–carbon double bond. Si, C(1), C(2), C(3), and the niobium atom all lie in a plane. If the coordination site of the alkyne is regarded as the axis of the roughly octahedral arrangement of ligands in **4d**, then the equatorial ligands are bent away from the alkyne. The remainder of the structure exhibits no unusual features.

The triad of chloride or bromide ligands found on the alkyne complexes described in this paper provide one with the opportunity to "fine tune" the niobium center via substitution with other ligands that can impart different electronic and/or steric effects. This is a highly desirable approach to the rational development of new and selective reagents and catalysts, and we therefore anticipate that this general class of compounds should prove to be valuable starting materials in the areas of organic and organometallic chemistry.

Experimental Section

Unless otherwise noted, all experiments were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres drybox or with use of standard Schlenk techniques. All solvents were purified and dried by standard techniques. All alkynes (except phenyl(*tert*-butyldimethylsilyl)acetylene) were obtained from commercially available sources and were distilled or recrystallized before use. Phenyl(*tert*-butyldimethylsilyl)acetylene was prepared by the reaction of PhC≡CLi (PhC≡CH, *n*-BuLi, THF, −78 °C) with $(t\text{-}Bu)Me_2SiCl$ in tetrahydrofuran. The product was isolated by Kugelrohr distillation; ca. 110 °C at 1 mm. $NbCl_5$ was purchased from either Aldrich Chemical Co. or Cerac. $NbBr_5$ was purchased from Cerac. $NbCl_3(DME)$ was prepared by a previously reported procedure.[4,5] Bu_3SnH was either purchased from commercial sources and distilled prior to use or prepared from $(Bu_3Sn)_2O$/polymethylhydrosiloxane.[9] In the latter case we recommend that Bu_3SnH be immediately redistilled after the initial distillation from the reaction mixture.

^1H (400 or 500 MHz) and ^{13}C (100.58 or 125.72 MHz) NMR spectra were recorded at 20–22 °C (unless otherwise noted). All resonances are reported in ppm relative to tetramethylsilane, and coupling constants are reported in Hz. Elemental analyses were performed by the Microanalytical Laboratory at the University of California, Berkeley, CA.

GC–MS data were acquired on a Hewlett-Packard 5970 MSD instrument using a 30-m DB-5 (J&W Scientific) capillary column.

Synthesis of $NbBr_3(DME)$ (2). A 1-L, three-neck flask was equipped with an overhead stirrer, an inlet for nitrogen gas, and a glass stopper. The flask was flame-dried while being purged with nitrogen gas and, when it was cooled to ambient temperature, was charged with dry dimethoxyethane (600 mL) and tributyltin hydride (59.0 g, 0.213 mol). Niobium pentabromide (50.0 g, 0.102 mol) was placed in a dry 250-mL round-bottom flask and then attached to a piece of latex tubing (30 cm in length, 1.8 cm in diameter) that was adapted with two male 24/40 joints on either end. An empty round-bottom flask was used to cap the addition apparatus. The glass stopper was removed from the reaction flask while the system was purged with nitrogen, and the aforementioned addition apparatus was quickly connected. The solution was cooled to ca. −78 °C (dry ice/2-propanol), and the solution was stirred vigorously while the $NbBr_5$ was added in portions over a 30-min period. (Note: vigorous stirring is essential to ensure that any $NbBr_5$ clinging near the top of the ground-glass joint is washed into the reaction mixture.) After the addition was complete, the reaction mixture was stirred with no further addition of dry ice to the cold bath. After 3.5 h the bath was removed and the reaction mixture was warmed to ambient temperature (ca. 1 h). During this time the heterogeneous reaction mixture turned from a brownish hue to a light purple. The mixture was filtered under an atmosphere of nitrogen (either in a drybox or with use of standard Schlenk techniques), and the resulting solid was washed with dimethoxyethane (2 × 150 mL) and pentane (2 × 150 mL) and dried in vacuo (4 h at 1 mm); 37.8 g (88%) of a bright purple, free-flowing solid was obtained: mp (sealed capillary) 130–160 °C dec; IR (cm^{-1}, Nujol mull) ν 1070, 1021, 1006, 978,

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[7] Cyclotrimerization of terminal alkynes employing niobium and/or tantalum compounds has been previously observed: (a) Lachmann, G.; DuPlessis, J. A. K.; DuToit, C. J. *J. Mol. Catal.* **1987**, *42*, 151. (b) Masuda, T.; Deng, Y.; Higashimura, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2798. (c) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233. (d) Dandliker, G. *Helv. Chim. Acta* **1969**, *52*, 1482. Also see ref 2.

[8] We have sometimes seen products arising from the ring opening of tetrahydrofuran.

[9] Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81.

845. Anal. Calcd for $C_4H_{10}Br_3O_2Nb$: C, 11.36; H, 2.38; Br, 56.70. Found: C, 11.34; H, 2.33; Br, 56.70; N, 0.00.

Synthesis of $(DME)X_3Nb(RC{\equiv}CR')$ (3). $NbX_3(DME)$ (17.3 mmol) was suspended in dichloromethane (60 mL), and the alkyne was added (17.3 mmol). The reaction mixture was stirred for 12 h and then filtered through a pad of Celite. The Celite was washed with dichloromethane, and the volatiles were removed from the filtrate in vacuo, leaving a dark oil or solid. The residue was dissolved in dichloromethane (30–60 mL), filtered, and pentane was added (5–10 mL). The solution was cooled to −30 °C, and the resulting crystalline complexes were isolated by filtration, washed with cold (ca. −30 °C) dichloromethane (15 mL) and then pentane (15 mL), and dried in vacuo. One or two more crops of crystals were isolated by removing the solvent from the mother liquors and repeating the above recrystallization process. Crystal color and shape (after washing and drying in vacuo[16]) and yields for the individual alkyne complexes listed in Table I are provided below (in parentheses), along with spectroscopic and analytical data. The carbon NMR spectrum for **3e** is fully assigned and is representative of the rest of the alkyne complexes **3**.

3a (orange needles, 84%): mp (sealed capillary) 161 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.98 (m, 4 H), 7.65–7.47 (m, 6 H), 4.34–4.31 (m, 2 H), 4.24–4.20 (m, 2 H), 4.11 (s, 3 H), 3.62 (s, 3 H); ^{13}C NMR (CD_2Cl_2) δ 210.8, 139.7, 132.9, 132.5, 130.9, 79.2, 73.3, 71.1, 66.8. Anal. Calcd for $C_{18}H_{20}Cl_3O_2Nb$: C, 46.23; H, 4.31. Found: C, 46.08; H, 4.23.

3b (brown cubes, 52%): mp (sealed capillary) 125–127 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.88 (d, J = 8.0, 2 H) 7.52 (m, 3 H), 4.27 (m, 2 H), 4.16 (m, 2 H), 4.03 (s, 3 H), 3.88 (q, J = 7.5, 2 H), 3.68 (s, 3 H), 1.51 (t, J = 7.5, 3 H); ^{13}C NMR (CD_2Cl_2) δ 215.6, 193.7, 139.9, 133.6, 132.7, 130.9, 78.9, 73.1, 71.3, 65.7, 34.6, 14.5. Anal. Calcd for $C_{14}H_{20}Cl_3O_2Nb$: C, 40.08; H, 4.80. Found: C, 40.01; H, 4.88.

3c (brown plates, 62%): mp (sealed capillary) 121–123 °C dec; ^{1}H NMR (CD_2Cl_2) δ 4.23 (m, 2 H), 4.10 (m, 2 H), 3.94 (s, 3 H) 3.81 (s, 3 H), 3.50 (q, J = 7.4, 4 H) 1.36 (t, J = 7.4, 6 H); ^{13}C NMR (CD_2Cl_2) δ 195.5, 78.7, 73.0, 71.0, 65.6, 34.3, 15.4. Anal. Calcd for $C_{10}H_{20}Cl_3O_2Nb$: C, 32.33; H, 5.44. Found: C, 32.31; H, 5.44.

3d (red needles, 51%): mp (sealed capillary) 145–155 °C dec; ^{1}H NMR (CD_2Cl_2) δ 4.22 (m, 2 H), 4.13 (m, 2 H), 3.97 (s, 3 H), 3.81 (s, 3 H), 3.11 (s, 6 H); ^{13}C NMR (CD_2Cl_2) δ 215.0, 79.5, 76.0, 68.5, 62.5, 23.6. Anal. Calcd for $C_8H_{16}Cl_3O_2Nb$: C, 27.97; H, 4.70. Found: C, 27.62; H, 4.54.

3e (black plates, 66%): mp (sealed capillary) 136–137 °C dec; ^{1}H NMR (CD_2Cl_2) δ 12.29 (s, 1 H), 3.78 (m, 4 H), 3.54 (s, 3 H), 3.49 (s, 3 H), 0.46 (s, 9 H); ^{13}C NMR (CD_2Cl_2) δ 223.4 ($H\mathit{C}{\equiv}CSiMe_3$), 200.8 ($HC{\equiv}\mathit{C}SiMe_3$), 76.4 (DME CH_2's), 71.9 (DME CH_2's), 68.8 (DME CH_3's), 63.1 (DME CH_3's), 0.1 ($-SiMe_3$). Anal. Calcd for $C_9H_{20}Cl_3O_2SiNb$: C, 27.89; H, 5.20. Found: C, 28.24; H, 5.15.

3f (black plates, 71%): mp (sealed capillary) 108–112 °C dec; ^{1}H NMR (CD_2Cl_2) δ 4.21 (dd, 2 H), 4.08 (dd, 2 H), 3.92 (s, 3 H), 3.76 (s, 3 H), 3.42 (t, J = 7.6, 2 H), 1.78 (m, 2 H), 1.01 (t, J = 7.3, 3 H), 0.32 (s, 9 H); ^{13}C NMR (CD_2Cl_2) δ 196.7, 189.2, 77.8, 72.2, 70.1, 63.8, 43.8, 24.6, 15.7, 1.0 (J_{C-Si} = 26.7). Anal. Calcd for $C_{12}H_{26}Cl_3O_2SiNb$: C, 33.55; H, 6.09. Found: C, 33.28; H, 6.09.

3g (brown plates, 67%): mp (sealed capillary) 128–133 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.81 (d, J = 7.1, 2 H), 7.50 (dt, J = 7.1, 7.4, 2 H), 7.39 (d, J = 7.4, 1 H), 4.25 (m, 4 H), 4.17 (s, 3 H), 3.56 (s, 3 H), 0.93 (s, 9 H), 0.51 (s, 6 H); ^{13}C NMR (CD_2Cl_2) δ 196.1, 180.7, 143.7, 131.7, 131.6, 130.0, 79.1, 72.9, 71.4, 65.7, 29.4, 21.2, −1.60 (J_{C-Si} = 26.7). Anal. Calcd for $C_{18}H_{30}Br_3O_2SiNb$: C, 33.83; H, 4.72. Found: C, 34.13; H, 4.60.

3h (golden plates, 83%): mp (sealed capillary) 153–155 °C dec; ^{1}H NMR (CD_2Cl_2) δ 4.20 (s, 4 H), 4.08 (s, 3 H), 3.66 (s, 3 H), 3.62 (q, ^3J = 7.5, 4 H), 1.36 (t, ^3J = 7.5, 6 H); ^{13}C NMR (CD_2Cl_2) δ 186.1, 78.8, 72.8, 70.9, 65.2, 36.6, 15.2. Anal. Calcd for $C_{10}H_{20}Br_3O_2Nb$: C, 23.79; H, 3.99. Found: C, 23.63; H, 3.94.

Synthesis of $(THF)_2Cl_3Nb(RC{\equiv}CR')$ (4). $NbCl_3(DME)$ (2.0 g, 6.9 mmol) was suspended in tetrahydrofuran (75 mL), and the alkyne was added (6.9 mmol). A reflux condenser was attached to the reaction flask, and the mixture was stirred and brought to a gentle reflux for 10 h. The reaction mixture was cooled to room temperature and then filtered through a pad of Celite. The Celite was washed with tetrahydrofuran (10 mL), and the volatiles were removed from the filtrate in vacuo, leaving a dark oil. The residue was dissolved in tetrahydrofuran (ca. 10 mL), the solution was filtered through a short plug of Celite, and pentane (5 mL) was added. Crystals were obtained upon cooling the solution to −30 °C. These were isolated by filtration, washed with a cold (ca. −30 °C) mixture of tetrahydrofuran/pentane (1:1, 5 mL), and dried in vacuo. One or two more crops of crystals were isolated by removing the solvent from the mother liquors and repeating the above recrystallization process. Crystal color and shape (after washing and drying in vacuo) and yields for the individual alkyne complexes listed in Table I are provided below (in parentheses), along with spectroscopic and analytical data. Repeated attempts at obtaining acceptable elemental analysis data for compounds **4a–d** have met with failure. Values for carbon and hydrogen are consistently low, suggesting that at least one tetrahydrofuran ligand is being lost upon pumping on the crystals in vacuo. The carbon NMR spectrum for **4d** is fully assigned and is representative of the rest of the alkyne complexes **4**.

4a (red needles, 57%): mp (sealed capillary) 115 °C dec; ^{1}H NMR (CD_2Cl_2) δ 4.25 (m, 8 H), 3.50 (s, 6 H), 2.03 (m, 8 H); ^{13}C NMR (CD_2Cl_2) 198.7, 71.1, 25.7, 21.0.

4b (red cubes, 65%): mp (sealed capillary) 162–168 °C dec; ^{1}H NMR (CD_2Cl_2, 22 °C) δ 7.79 (m, 2 H), 7.51 (m, 2 H), 7.42 (m, 1 H), 4.64 (m, 8 H), 3.81 (q, J = 7.2, 2 H), 1.95 (m, 8 H), 1.45 (t, ^3J = 7.2, 3 H); ^{1}H NMR (CD_2Cl_2, −80 °C) δ 7.70 (d, J = 7.2, 2 H), 7.50 (dd, J = 7.2, 7.2, 2 H), 7.46 (d, J = 7.2, 1 H), 4.30 (m, 4 H), 4.01 (m, 4 H), 3.72 (q, J = 7.4, 2 H), 1.94 (m, 8 H), 1.35 (t, J = 7.4, 3 H); ^{13}C NMR (CD_2Cl_2, 22 °C) δ 214.1, 192.4, 140.1, 133.2, 132.3, 130.8, 75.0, 34.9, 27.8, 14.6; ^{13}C NMR (CD_2Cl_2, −80 °C) δ 227.5, 205.0, 137.4, 133.4, 132.1, 130.2, 78.8, 73.4, 34.6, 27.8, 26.8, 14.1.

4c (red cubes, 52%): mp (sealed capillary) 131–137 °C dec; ^{1}H NMR (CD_2Cl_2) δ 3.61 (m, 8 H), 3.03 (s, 3 H), 1.76 (m, 8 H), 1.36 (s, 9 H); ^{13}C NMR (CD_2Cl_2) δ 206.2, 181.5, 72.3, 49.1, 34.4, 31.3, 28.9.

4d (ruby cubes, 55%): mp (sealed capillary) 116 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.66 (m, 2 H), 7.46 (m, 2 H), 7.34 (m, 1 H), 4.04 (bs, 8 H), 1.90 (bs, 8 H), 0.91 (s, 9 H), 0.42 (s, 6 H); ^{13}C NMR (CD_2Cl_2) δ 213.2 ($Ph\mathit{C}{\equiv}C$), 187.2 (($\equiv\mathit{C}Si(t\text{-}Bu)Me_2$), 143.3 ($C_{ipso}$ Ph), 130.8, 129.7, 129.5 (Ph's), 73.9 ($\mathit{C}H_2O\mathit{C}H_2$, THF's), 27.0 ($\mathit{C}H_2\mathit{C}H_2$, THF's), 20.5 ($Me_3\mathit{C}Si-$), −2.39 ($\mathit{Me}_3CSi-$), −2.54 ($\mathit{Me}_2Si-$).

Catalytic Cyclotrimerization of 1-Hexyne with $NbCl_3(DME)$. A 250-mL flask was charged with 1-hexyne (5.0 g, 61 mmol) and dichloromethane (75 mL), and $NbCl_3(DME)$ (0.88 g, 3.0 mmol) was added while the reaction mixture was stirred. The mixture became warm at this point. After it was stirred for 12 h, the reaction mixture was poured into a separatory funnel and hydrolyzed with aqueous potassium hydroxide (10% w/v, 75 mL) and the organic layer separated. The solution was extracted with ether (3 × 150 mL), the organics were combined, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo, leaving a pale yellow oil. This material was purified by Kugelrohr distillation (ca. 50 °C, 1 mm) to give 4.36 g (87%) of a 1:1 mixture of 1,2,4- and 1,3,5-tributylbenzenes. The spectroscopic data reported are for a ca. 1:1 mixture of the two tributylbenzenes:[7b] ^{1}H NMR ($CDCl_3$) δ 7.16 (d), 7.05 (m), 6.92 (s), 2.65 (m), 1.63 (m), 1.48 (m), 1.02 (m); ^{13}C NMR ($CDCl_3$) δ 143.0, 140.6, 140.4, 137.9, 129.5, 129.3, 126.1, 126.0, 36.0, 35.7, 34.2, 34.1, 32.8, 32.4, 23.3, 23.2, 22.91, 22.88, 14.41, 14.37; MS (m/z) 246 (M^+, 24), 203 (27), 161 (100), 147 (17), 119 (20), 105 (27), 91 (19).

X-ray Crystal Structure Determination of 4d. Details of the data collection and refinement are summarized in Table III. Dark red platelike crystals of **4d** were obtained by slow crystallization from tetrahydrofuran/pentane (2:1). *These crystals were not dried in vacuo.* Fragments cleaved from some of these crystals were mounted in thin-wall glass capillaries in an inert-atmosphere box and then flame-sealed. Preliminary precession photographs indicated monoclinic Laue symmetry and yielded approximate cell dimensions. The crystal used for data collection was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. Automatic peak search and indexing procedures yielded the monoclinic reduced primitive cell. The final cell parameters and specific data collection parameters for this data set are given in Table III.

The 3787 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects.[10–12] No correction

Table II. Selected Bond Lengths (Å) and Angles (deg) for (THF)$_2$Cl$_3$Nb(PhC$\equiv$CSi(*t*-Bu)Me$_2$) (4d)

Bond Lengths

Nb–C(1)	2.069 (2)	Nb–O(1)	2.345 (2)
Nb–C(2)	2.067 (2)	Nb–O(2)	2.226 (2)
C(1)–C(2)	1.306 (3)	Nb–Cl(1)	2.411 (1)
C(1)–Si	1.873 (2)	Nb–Cl(2)	2.371 (1)
C(2)–C(3)	1.481 (3)	Nb–Cl(3)	2.429 (1)

Bond Angles

Si–C(1)–C(2)	146.48 (21)	Cl(1)–Nb–Cl(3)	158.67 (3)
C(1)–C(2)–C(3)	137.19 (24)	Cl(1)–Nb–O(1)	80.13 (5)
Cl(1)–Nb–C(1)	84.70 (7)	Cl(1)–Nb–O(2)	81.73 (5)
Cl(1)–Nb–C(2)	109.30 (7)	O(1)–Nb–O(2)	80.18 (6)
Cl(1)–Nb–Cl(2)	99.58 (3)		

for crystal decomposition was necessary. Inspection of the azimuthal scan data[13] showed the variation $I_{\min}/I_{\max} = 0.92$ for the average curve. An empirical correction based on the observed variation was applied to the data. Inspection of the systematic absences indicated uniquely space group $P2_1/c$. Removal of systematically absent and redundant data left 3434 unique data in the final data set.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. In a difference Fourier map calculated by following the refinement of all nonhydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of the most of the hydrogen atoms. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.3 times the B_{eqv} values of the atoms to which they were attached. They were included in structure factor calculations but not refined. In the final cycles of refinement two reflections suffering from apparent secondary extinction were removed from the refinement.

The final residuals for 262 variables refined against the 2768 data for which $F^2 > 3\sigma(F^2)$ were $R = 2.41\%$, $R_w = 3.28\%$, and GOF = 1.594. The R value for all 3434 data was 5.12% (see footnote c of Table III).

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor (see footnote c of Table III), used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used,[14] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[15]

Table III. Summary of Crystal Data and Data Collection Parameters for (THF)$_2$Cl$_3$Nb(PhC$\equiv$CSi(*t*-Bu)Me$_2$) (4d)

Crystal Parameters at T = 25 °C^{a,b}

mol formula	C$_{22}$H$_{36}$Cl$_3$O$_2$SiNb	α, deg	90.0
fw	559.9	β, deg	114.122 (8)
space group	$P2_1/c$	γ, deg	90.0
size, mm	0.10 × 0.30 × 0.45	V, Å^3	2633.8 (11)
a, Å	14.9241 (16)	Z	4
b, Å	11.9364 (18)	ρ(calcd), g cm^{-3}	1.41
c, Å	16.1998 (19)	μ(calcd), cm^{-1}	8.0

Data and Measurement Parameters^c

radiation	Mo Kα (λ = 0.71073 Å)
monochromator	highly-oriented graphite (2θ = 12.2°)
detector	crystal scintillation counter, with PHA
rflns measd	$+h,+k,\pm l$
2θ range, deg	3–45
scan type	θ–2θ
scan width	$\Delta\theta = 0.55 + 0.35 \tan\theta$
scan speed (θ), deg min^{-1}	0.83–6.70
bkgd	measd over 0.25 ($\Delta\theta$) added to each end of the scan
vert aperture, mm	3.0
horiz aperture, mm	$2.0 + 1.0 \tan\theta$
no. of reflns collected	3787
no. of unique rflns	3434
R,^{d} %	5.12
R_w,^{d} %	3.28
GOP^d	1.594

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 26° and 32°. [b] In this table the esd's of all parameters are given in parentheses, right justified to the least significant digit(s) of the reported value. [c] Data were collected on an Enraf-Nonius CAD-4 diffractometer. Intensity standards (372), (920), and (1,3,10) were measured every 1 h of X-ray exposure time. Over the data collection period no decrease in intensity was observed. [d] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$, $R_w = [(\sum w(|F_o| - |F_c|)^2)/\sum wF_o^2]^{1/2}$, and GOF $= [(\sum w(|F_o| - |F_c|)^2)/(n_o - n_v)]^{1/2}$ where n_o is the number of observations, n_v the number of variable parameters, and the weights w were given by $w = 1/[\sigma^2(F_o)]$ $(\sigma(F_o^2) = [\sigma^2\sigma^2(F_o^2) + (pF^2)^2]^{1/2}$, where $\sigma^2(F_o)$ is calculated as above from $\sigma(F_o^2)$ and where p is the factor used to lower the weight of intense reflections.

Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.35 e/Å^3, and the lowest excursion was −0.24 e/Å^3. Both were located near the niobium atom. There was no indication of secondary extinction in the high-intensity low-angle data.

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Registry No. 1, 110615-13-9; **2**, 126083-88-3; **3a**, 126083-89-4; **3b**, 126083-90-7; **3c**, 126083-91-8; **3d**, 126083-92-9; **3e**, 126083-93-0; **3f**, 126083-94-1; **3g**, 126083-95-2; **3h**, 126083-96-3; **4a**, 126083-97-4; **4b**, 126083-98-5; **4c**, 126083-99-6; **4d**, 126084-00-2; PhC$\equiv$CPh, 501-65-5; PhC$\equiv$CEt, 622-76-4; EtC$\equiv$CEt, 928-49-4; MeC$\equiv$CMe, 503-17-3; Me$_3$SiC$\equiv$CH, 1066-54-2; Me$_3$SiC$\equiv$CPr, 18270-17-2; PhC$\equiv$CSi(Me)$_2$CMe$_3$, 85443-40-9; Me$_3$CC$\equiv$CMe, 999-78-0; niobium pentabromide, 13478-45-0; tributyltin hydride, 688-73-3; 1-hexyne, 693-02-7; 1,2,4-tributylbenzene, 14800-16-9; 1,3,5-tributylbenzene, 841-07-6.

Supplementary Material Available: Tables of atomic positional and thermal parameters of the non-hydrogen atoms, anisotropic thermal parameters and the positional and thermal parameters of the hydrogen atoms, and bond distances and angles (6 pages); a listing of the values of F_o and F_c (20 pages). Ordering information is given on any current masthead page.

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(10) Calculations were performed on a DEC Microvax II computer using locally modified Nonius-SDP[3] software operating under the Micro-VMS operating system.

(11) *Structure Determination Package User's Guide*; B. A. Frenz: College Station, TX 77840, 1985.

(12) The data reduction formulas are

$$F_o^2 = \frac{w}{Lp}(C - 2B)$$

$$\sigma_o(F_o^2) = \frac{w}{Lp}(C + 4B)^{1/2}$$

$$F_o = (F_o^2)^{1/2}$$

$$\sigma_o(F) = (F_o^2 + \sigma_o(F_o)^2)^{1/2} - F_o$$

where C is the total count in the scan, B is the sum of the two background counts, σ is the scan speed used in deg/min, and

$$\frac{1}{Lp} = \frac{(\sin 2t)(1 + \cos^2 2\theta_m)}{1 + \cos^2 2\theta_m - \sin 2\theta}$$

is the correction for Lorentz and polarization effects for a reflection with scattering angle 2θ and radiation monochromatized with a 50% perfect single-crystal monochromator with scattering angle $2\theta_m$.

(13) Reflections used for azimuthal scans were located near χ = 90°, and the intensities were measured at 10° increments of rotation of the crystal about the diffraction vector.

(14) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(15) Cromer, D. T. In ref 14, Table 2.3.1.

(16) All of the alkyne complexes reported below are highly crystalline and intensely colored in solution. When they are washed and dried, they typically lose their luster.

(17) Two analogous structures have appeared since acceptance of this paper; see: Cotton, F. A.; Shang, M. *Inorg. Chem.* **1990**, *29*, 508.