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Reactions of the Trimetallic Neopentylidyne Complex $[\{Cl_2(MeOCH_2CH_2OMe)Ta(\mu\text{-}CCMe_3)\}_2Zn(\mu\text{-}Cl)_2]$ with Alkynes. A Structural Study of $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_2(CH_2CMe_2CH_2)_2)TaCl_2]$

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The reaction between the dimeric tantalum alkylidyne complex $[\{Cl_2(MeOCH_2CH_2OMe)Ta(\mu\text{-}CCMe_3)\}_2Zn(\mu\text{-}Cl)_2]$ and acetylenes ($R^1C{\equiv}CR^2$) leads to products in which two acetylene molecules and one alkylidyne moiety have formed a cyclopentadienyl ligand. Thus, in inert solvents the complexes $[(\eta^5\text{-}C_5(t\text{-}Bu)(R^1)_2(R^2)_2)TaCl_2(R^1C{\equiv}CR^2)]$ are formed, whereas in chlorinated solvents the complexes $[(\eta^5\text{-}C_5(t\text{-}Bu)(R^1)_2(R^2)_2TaCl_4]$ are formed. The reaction of the alkylidyne complex with dineopentylacetylene yields the complexes $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_3(CH_2CMe_2CH_2))TaCl_3]$ and $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_2(CH_2CMe_2CH_2)_2)TaCl_2]$, in which respectively one and two neopentyl substituents on the cyclopentadienyl ligand have been intramolecularly metalated. The latter complex crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with $a = 15.197$ (5) Å, $b = 17.276$ (5) Å, $c = 11.273$ (3) Å, $\beta = 90.74$ (3)°, $U = 2959.4$ (1.5) Å^3, and $D_{calcd} = 1.46$ g·cm^{-3} for $Z = 4$ and $M = 651.6$. The coordination of the tantalum falls into the $CpML_4$ class, but, unlike all previously crystallographically characterized complexes of this type, the coordination geometry is of the 3.3.1 rather than the 3.4 type.

Introduction

To our knowledge, reactions of tantalum neopentylidyne complexes with alkynes have not been reported before, although a number of such complexes are available.[1] We have recently described the synthesis and crystal structure of the trinuclear neopentylidyne complex $[\{Cl_2(MeOCH_2CH_2OMe)Ta(\mu\text{-}CCMe_3)\}_2Zn(\mu\text{-}Cl)_2]$, **1**, in which two $Cl_2(MeOCH_2CH_2OMe)Ta{\equiv}CCMe_3$ species are stabilized by interaction with $ZnCl_2$.[2] In the following we report on the reaction of this alkylidyne complex with internal and terminal alkynes.

Results

When the dimeric tantalum alkylidyne complex $[\{Cl_2(MeOCH_2CH_2OMe)Ta(\mu\text{-}CCMe_3)\}_2Zn(\mu\text{-}Cl)_2]$, **1**, is suspended in 2-butyne, it slowly dissolves from the pink suspension to give a solution of the yellow cyclopentadienyl complex $[(\eta^5\text{-}C_5(t\text{-}Bu)(Me)_4)TaCl_2(MeC{\equiv}CMe)]$, **2a**, which is isolated in ~80% yield[3] (cf. Scheme I).[4]

Apparently two butyne molecules have reacted with one alkylidyne moiety to form the tetramethyl-*tert*-butylcyclopentadienyl ligand. In a similar way **1** reacts with 3,3-dimethyl-1-butyne in THF to give $[(\eta^5\text{-}C_5H_2(t\text{-}Bu)_3)TaCl_2(Me_3CC{\equiv}CH)]$, **2d** (only one isomer with respect to cyclopentadienyl substitution is obtained).

In the presence of chlorinated solvents the reaction takes a slightly different course. Thus, when **1** is reacted with 4 mol of 2-butyne in dichloromethane, the yellow cyclopentadienyltantalum(V) tetrachloro complex $[(\eta^5\text{-}C_5(t\text{-}Bu)(Me)_4)TaCl_4]$, **3a**, is formed in ~70 % yield instead of the 2-butyne adduct **2a** (cf. Scheme I). In an analogous procedure the complexes $[(\eta^5\text{-}C_5(t\text{-}Bu)(Et)_4)TaCl_4]$, **3b**, and $[(\eta^5\text{-}C_5(t\text{-}Bu)(n\text{-}Pr)_4)TaCl_4]$, **3c**, are obtained by reacting **1** with 3-hexyne and 4-octyne, respectively.

Terminal alkynes react with **1** to give cyclopentadienylTa^VCl_4 complexes when a 1:1 mixture of dichloromethane and carbon tetrachloride is used as a solvent. Thus we have been able to prepare $[(\eta^5\text{-}C_5H_2(t\text{-}Bu)_3)TaCl_4]$, **3d**, and $[(\eta^5\text{-}C_5H_2(i\text{-}Bu)_2(t\text{-}Bu))TaCl_4]$, **3e**, by reaction of **1** with 3,3-dimethyl-1-butyne and 4-methyl-1-pentyne, respectively. In the former case only one isomer with respect to cyclopentadienyl ligand substitution is obtained; in the latter case two isomers **3e′** and **3e″** are formed in a 35:65 ratio (cf. Scheme I).

When **1** is reacted with terminal acetylenes in pure dichloromethane, the yields of the $CpTaCl_4$ products are strongly diminished. Thus, when **1** is reacted with 3,3-dimethyl-1-butyne in dichloromethane, we observed a new complex which is formed together with the oxidation

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(1) (a) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 2935. (b) McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962. (c) *Ibid.* **1980**, *102*, 6608.

(2) Gal, A. W.; Van der Heijden, H. *J. Chem. Soc., Chem. Commun.* **1983**, 420.

(3) In this case appreciable amounts of hexamethylbenzene were formed.

(4) Proof of the structure of all complexes has been obtained from their ^1H NMR and ^{13}C NMR spectra (cf. Table I) and from desorption chemical ionization (DCI)[5] mass spectrometry using pulsed positive negative chemical ionization (PPNICI)[6] (cf. Table II). The presence of a η^5-cyclopentadienyl ligand in **2a**, **2d**, and **3a–e** is easily established by comparison of the NMR spectroscopic data with those of the known complexes $[(\eta^5\text{-}C_5Me_5)TaCl_4]$ and $[(\eta^5\text{-}C_5Me_5)TaCl_2(MeC{\equiv}CMe)]$.[7] Assignment of the ^{13}C NMR resonances was based on fully coupled, gated decoupled, or off-resonance-decoupled spectra. To ascertain the assignments for **3e**, **6**, and **7**, additional *J*-modulated spin-echo techniques and selective decoupling were applied. CH coupling constants are only reported for anomalous cases; all other coupling constants are in the range of 125–130 Hz, the normal value for sp^3 carbon–proton bonds. The purity of the complexes was checked by microanalytical techniques (cf. Experimental Section).

(5) Cotter, R. J. *Anal. Chem.* **1980**, *52*, 1589A.

(6) Hunt, D. F.; Stafford, G. C., Jr.; Crow, F. W.; Russel, J. W. *Anal. Chem.* **1976**, *48*, 2098.

(7) (a) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558. (b) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387.

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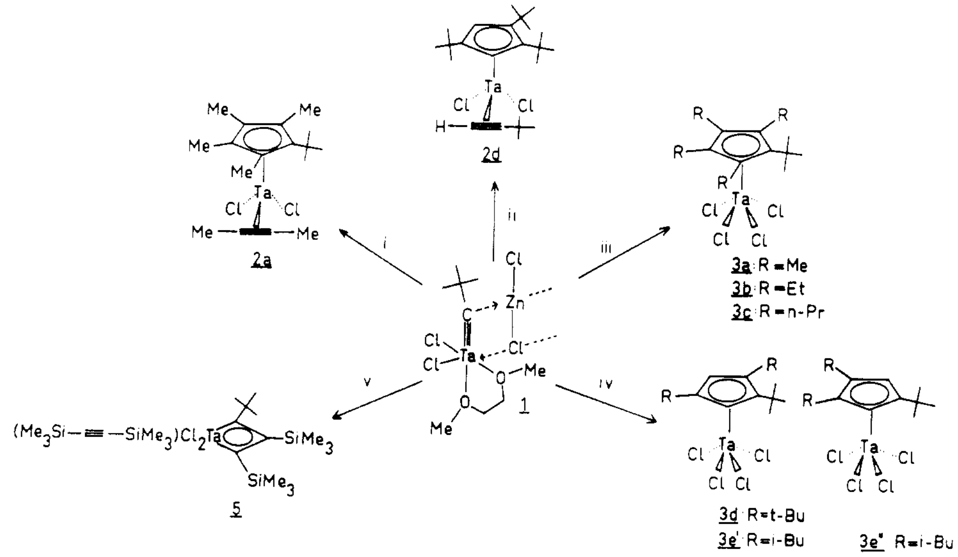
Scheme I



i, 2-butyne, neat, 25 °C; ii, 3,3-dimethyl-1-butyne, toluene, 25 °C; iii, RC≡CR, CH_2Cl_2, 25 °C; iv, RC≡CH, CCl_4/CH_2Cl_2 (1:1), 25 °C; v, bis(trimethylsilyl)acetylene, CH_2Cl_2, 25 °C.

product **3d** in a 5:3 ratio. The mass spectroscopic data for this complex **4** give an empirical molecular formula ($C_{20}H_{32}TaCl_3$), which indicates that its hydrocarbon fragment(s) cannot result from a simple combination of alkylidyne and alkyne fragments. Furthermore the NMR data give strong indications that at least one solvent molecule is involved in the formation of the hydrocarbon ligand.[8] The exact structure of this product is not known at this point.

The formation of cyclopentadienyl ligands from the alkylidyne moiety in **1** and two molecules of an alkyne was found to be a general reaction for both internal and terminal alkynes. It was found, however, that the sterically very demanding 2,2,5,5-tetramethyl-3-hexyne does not react with **1**. Furthermore, when **1** was reacted with the bulky bis(trimethylsilyl)acetylene, we obtain a product with empirical formula $[TaCl_2(CCMe_3)(Me_3SiC{\equiv}CSiMe_3)_2]$, but in which the alkyne and alkylidyne fragments have not been combined to a cyclopentadienyl ligand, as becomes evident from the ^{13}C NMR data. Comparison of these data with those of the tungsten metallacyclobutadiene complex $[(\eta^5\text{-}C_5H_5)W\{C(Me)C(t\text{-}Bu)C(Me)\}Cl_2]$[9] shows that this complex is likely to be the tantalacyclobutadiene complex $[(Me_3SiC{\equiv}CSiMe_3)TaCl_2\{C(t\text{-}Bu)C(SiMe_3)C(SiMe_3)\}]$, **5**. Thus, for **5** resonances are found at δ 187.4 and 196.3 for the two α-carbon atoms of the tantalacyclobutadiene ring and at δ 120.7 for the β-carbon atom, while for the tungsten complex these resonances are found at δ 244.3 and 120.4, respectively (cf. Table I).

When **1** is reacted with 2,2,7,7-tetramethyl-4-octyne (dineopentylacetylene), hydrogen is evolved and we obtain, instead of the expected product $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_4)TaCl_2(Me_3CCH_2C{\equiv}CCH_2CMe_3)]$, a yellow complex with the empirical formula $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_4)TaCl_2$ minus 2H]. The same product is formed when the reaction is performed in dichloromethane, but in addition a red complex with the empirical formula $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_4)TaCl_3$ minus H] was isolated as a minor byproduct. The presence of a cyclopentadienyl ligand in both complexes was again inferred from the ^{13}C NMR spectra. Further inspection of the spectroscopic data led to the tentative assignment of the monometalated structure **6** to the red complex and of the bismetalated structure **7** to the yellow complex (in both cases only one isomer with respect to the cyclopentadienyl ligand substitution was obtained; the exact substitution pattern could not be inferred from the spectral data (cf. Table III)).

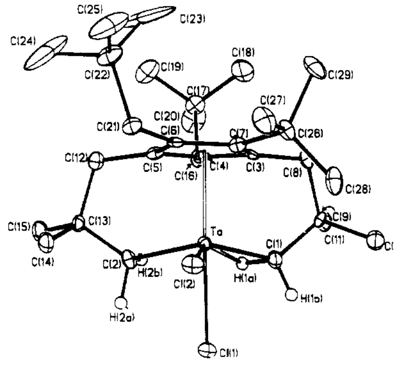
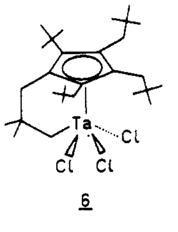


Figure 1. The molecular structure and crystallographic labeling schemes for $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_2(CH_2CMe_2\overline{CH_2)_2)T}aCl_2]$, **7**, showing 50% probability ellipsoids, hydrogen atoms of all methyl groups, and all but the metal-bonded methylene groups have been omitted for clarity.



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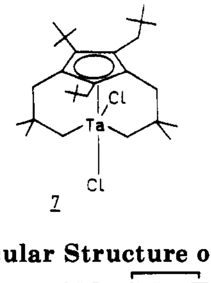

7

Crystal and Molecular Structure of $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_2(CH_2CMe_2\overline{CH_2)_2T}aCl_2]$, 7

The structure of **7** was determined by an X-ray diffraction study carried out at 200 K using a single crystal obtained from dichloromethane solution. The resultant bond lengths and interbond and torsion angles are listed in Tables IV and V. The molecular geometry is illustrated in Figure 1, which shows the labeling scheme adopted, and

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[8] When the reaction is performed in deuterated dichloromethane, the resonance at δ 3.41 (relative intensity 2) is removed from the ^1H NMR spectrum, whereas the signal at δ 7.97 (relative intensity 1), which originally appears as a doublet, now appears as a singlet.

[9] Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* 1983, 2, 1046.

Table I. ^{1}H NMR and ^{13}C NMR Spectroscopic Data of Compounds 2a, 2d, 3a–e, 4, and 5[a]

compd		
2a	^{1}H NMR (C_6D_6)	1.26 (Me_3C), 1.72 and 2.09 (MeCp), 2.66 (MeC$\equiv$)
	^{13}C NMR (CD_2Cl_2)	32.02 (Me_3C), 36.06 (Me_3C), 12.32 and 15.54 (MeCp), 21.74 (MeC$\equiv$), 130.5 (*Cp*-*t*-Bu), 122.00 and 122.12 (*Cp*Me), 229.86 (MeC$\equiv$)
2d	^{1}H NMR (CD_2Cl_2)	1.37 (Me_3C, 18 H), 1.18 (Me_3C, 9 H), 0.98 (Me_3CC$\equiv$), 6.23 (*H*Cp), 12.63 (*H*C$\equiv$)
	^{13}C NMR ($CDCl_3$)	31.0, 31.1, and 33.5 (Me_3C, relative intensity 1:1:2), 33.6 and 35.7 ($\mathrm{Me_3}C$Cp, relative intensity 1:2); 44.8 ($\mathrm{Me_3}C$C$\equiv$); 109.3 (CpH, J_{CH} = 172 Hz), 135.1 and 138.4 (*Cp*CMe$_3$, relative intensity 1:2), 217.9 ($\equiv$CH, J_{CH} = 187 Hz), 247.7 ($\equiv$*C*CMe$_3$)
3a	^{1}H NMR (C_6D_6)	1.25 (Me_3C), 2.17 and 2.50 (MeCp)
	^{13}C NMR (C_6D_6)	31.04 (Me_3C), 37.68 ($\mathrm{Me_3}C$), 13.98 and 17.18 (MeCp), 143.37 (*Cp*-*t*-Bu), 131.70 and 134.59 (*Cp*Me)
3b	^{1}H NMR (CD_2Cl_2)	1.63 (Me_3C), 3.14 ($\mathrm{CH_3C}H_\mathrm{A}\mathrm{H_B}$, dq, $^2J_{AB}$ = 15 Hz, ^3J = 7.5 Hz), 3.37 ($\mathrm{CH_3CH_A}H_\mathrm{B}$), 1.36 ($\mathrm{C}H_3\mathrm{CH_AH_B}$, t); 3.02 ($\mathrm{CH_3C}H_2$, quart), 1.28 ($\mathrm{C}H_3\mathrm{CH_2}$, t)
	^{13}C NMR (CD_2Cl_2)	39.30 ($\mathrm{Me_3}C$), 32.26 (Me_3C), 23.07 and 24.25 ($C\mathrm{H_2CH_3}$); 16.91 and 16.31 ($\mathrm{CH_2}C\mathrm{H_3}$), 145.77 (*Cp*-*t*-Bu), 138.35 and 140.44 (*Cp*Et)
3c	^{1}H NMR (CD_2Cl_2)	1.60 (Me_3C), 2.6–3.6 ($\mathrm{C}H_2\mathrm{CH_2CH_3}$), 1.1–2.1 ($\mathrm{CH_2C}H_2\mathrm{CH_3}$); 1.09 ($\mathrm{CH_2CH_2C}H_3$, t, J = 7 Hz)
	^{13}C NMR (CD_2Cl_2)	31.6 (Me_3C), 38.6 ($\mathrm{Me_3}C$), 14.3 and 14.5 ($C\mathrm{H_3CH_2}$); 24.9 and 25.3 ($\mathrm{CH_3}C\mathrm{H_2}$), 31.9 and 33.3 ($C\mathrm{H_2Cp}$) 136.4 and 138.5 (*Cp*CH$_2$), 144.8 (*Cp*CMe$_3$)
3d	^{1}H NMR (CD_2Cl_2)	1.38 (Me_3C, 9 H), 1.56 (Me_3C, 18 H), 6.72 (*H*Cp)
	^{13}C NMR (CD_2Cl_2)	36.4 ($\mathrm{Me_3}C$), 30.2 (Me_3C), 37.7 ($\mathrm{Me_3}C$), 32.8 (Me_3C); 119.2 (*Cp*H, J_{CH} = 178 Hz), 148.9 and 153.0 (*Cp*-*t*-Bu)
3e[b]	^{1}H NMR (C_7D_8)	6.28 (*H*–Cp, **3e″**), 5.87 and 6.20 (*H*–Cp, d, J = 2.5 Hz, **3e′**)
	^{13}C NMR ($CDCl_3$)	**3e″**: 152.9 (*Cp*-*t*-Bu), 137.6 (*Cp*-*i*-Bu), 118.2 (*Cp*H) **3e′**: 148.3 (*Cp*-*t*-Bu), 136.5 and 139.7 (*Cp*-*i*-Bu); 119.7 and 123.3 (*Cp*H)
4	^{1}H NMR ($CDCl_3$)	1.20 (s, 9 H), 1.51 (s, 18 H), 3.41 (t, 2 H, J = 3.5 Hz), 6.90 (s, 2 H), 7.97 (d, 2 H)
5	^{1}H NMR (CD_2Cl_2)	0.93 (Me_3C), 0.32 (Me_3Si, 18 H), 0.35 (Me_3Si, 18 H)
	^{13}C NMR (CD_2Cl_2)	0.90 (Me_3Si), 1.01 (Me_3Si), 33.0 (Me_3C), 37.7 ($\mathrm{Me_3}C$); 120.7 (*C*Me$_3$Si), 187.4 and 196.3 (Ta*C*), 263.3 ($\mathrm{Me_3Si}C\equiv$)

[a] Parts per million relative to Me_4Si; singlet unless otherwise indicated. [b] Mixture of two isomers, **3e′** and **3e″** (cf. Scheme I). Only the cyclopentadienyl carbon atom resonances are clearly resolved.

Figure 2, which shows a stereoscopic view of the molecule. The crystal structure consists of isolated molecules of 7 separated by normal van der Waals contacts, the shortest of which are H(11B)···H(2A)′ = 2.39 (9) Å[10] (H(2A)′ is related to H(2A) by $-x$, $1 - y$, $1 - z$) and H(28C)···Cl(1)′ = 2.90 (9) Å (Cl(1)′ is related to Cl(1) by $-x$, $1 - y$, $-z$).

Table II. PPNICI Mass Spectroscopic Data of Compounds 2a, 3a, and 4–7[a]

compound	[M + H]$^+$	[M + H – HCl]$^+$	[M]$^-$
2a	483 (100)	447 (70)	482 (100)
3a		463 (100)	498 (100)
4		523 (100)	558 (100)
5	661 (55)	625 (40)	660 (100)
6		651 (100)	686 (100)
7		615 (100)	650 (100)

[a] Reagent gas CH_4, m/z values (relative intensity %).

Table III. Relevant ^{1}H NMR and ^{13}C NMR Spectroscopic Data of Compounds 6 and 7[a]

compd		
6	^{1}H NMR (CD_2Cl_2)	1.62 (Me_3CCp), 1.20, 1.21, and 1.25 (Me_3CCH$_2$); 1.29 and 1.30 (Me_2C)
	^{13}C NMR (CD_2Cl_2)	34.4 and 38.7 ($\mathrm{TaCH_2C}Me_2$), 57.8 ($\mathrm{TaCH_2}C\mathrm{Me_2}$), 109.0 ($\mathrm{Ta}C\mathrm{H_2CMe_2}$), 129.7, 136.9, 142.2, and 143.5 (*Cp*, relative intensity 1:1:2:1)
7[b]	^{1}H NMR (C_6D_6)	0.33 (H(1a), dd, $J_{H(1a)H(1b)}$ = 14 Hz, $J_{H(1a)H(2a)}$ = 1 Hz), 2.01 (H(2a), dd, $J_{H(2a)H(2b)}$ = 15 Hz), 2.50 (H(2b)), 4.03 (H(1b))
	^{13}C NMR (CD_2Cl_2)	34.6, 36.8, 37.2, and 37.6 ($\mathrm{TaCH_2C}Me_2$), 50.9 and 59.0 ($\mathrm{TaCH_2}C\mathrm{Me_2}$), 103.0 and 119.4 ($\mathrm{Ta}C\mathrm{H_2CMe_3}$), 127.6 132.5, 132.9, and 134.3 (Cp, relative intensity 1:2:1:1)

[a] Parts per million relative to Me_4Si; singlet unless otherwise indicated. [b] Indices refer to atomic numbering in crystal structure (cf. Figure 1).

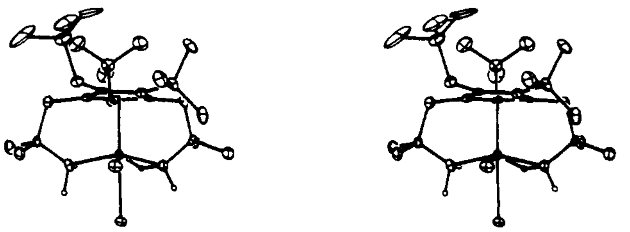

Figure 2. Stereoscopic view of 7 illustrating the molecular geometry.

The molecule consists of a central tantalum atom η^5-coordinated by a pentaalkylcyclopentadienyl (Cp) ligand and by two chloride ligands. The tantalum atom is further bonded to two of the alkyl substituents of the cyclopentadienyl ligand, these being the metalated neopentyl substituents as indicated on spectroscopic grounds (see above). As might be anticipated, the metalated neopentyl groups are not adjacent; thus they occupy the 2- and 4-positions relative to the *tert*-butyl substituent on the Cp ring. The non-metalated neopentyl groups are oriented so as to place their $C(Me)_3$ groups on the distal side of the Cp ring relative to the metal atom. Thus, the coordination of the tantalum falls into the $CpML_4$ class. Unlike all previously crystallographically characterized complexes of this type, the coordination geometry is of the 3.3.1 rather than the 3.4 type[11,12] (taking the Cp ligand to occupy three sites in the coordination sphere). Alternatively taking the Cp to occupy one site, the ligand geometry around tantalum in 7 may be conceived as approximately trigonal bipyramidal, in contrast to the usual square pyramidal.

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[10] Estimated standard deviations in the least significant digit are given in parentheses here and throughout this paper.

[11] Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1278 and footnote 12 of ref 12.

[12] Kubâcek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

Table IV. Bond Lengths and Angles for 7

Bond Lengths (Å)

Ta–Cl(1)	2.454 (2)	Ta–Cl(2)	2.362 (2)	C(6)–C(21)	1.526 (9)	C(7)–C(26)	1.560 (9)
Ta–C(1)	2.176 (7)	Ta–H(1a)	2.300 (76)	C(8)–C(9)	1.557 (9)	C(9)–C(10)	1.529 (9)
Ta–C(2)	2.215 (6)	Ta–C(3)	2.430 (6)	C(9)–C(11)	1.548 (9)	C(12)–C(13)	1.541 (9)
Ta–C(4)	2.452 (6)	Ta–C(5)	2.448 (6)	C(13)–C(14)	1.534 (9)	C(13)–C(15)	1.545 (9)
Ta–C(6)	2.530 (6)	Ta–C(7)	2.486 (6)	C (16)–C(17)	1.551 (9)	C(17)–C(18)	1.527 (11)
C(1)–H(1a)	1.102 (78)	C(1)–H(1b)	0.927 (64)	C(17)–C(19)	1.532 (10)	C(17)–C(20)	1.516 (11)
C(1)–C(9)	1.554 (9)	C(2)–H(2a)	1.064 (46)	C(21)–C(22)	1.578 (9)	C(22)–C(23)	1.483 (13)
C(2)–H(2b)	1.055 (52)	C(2)–C(13)	1.516 (9)	C(22)–C(24)	1.502 (14)	C(22)–C(25)	1.502 (11)
C(3)–C(4)	1.436 (9)	C(3)–C(7)	1.443 (9)	C(26)–C(27)	1.541 (10)	C(26)–C(28)	1.532 (10)
C(3)–C(8)	1.513 (9)	C(4)–C(5)	1.420 (9)	C(26)–C(29)	1.556 (10)		
C(4)–C(16)	1.511 (9)	C(5)–C(6)	1.422 (9)				
C(5)–C(12)	1.522 (9)	C(6)–C(7)	1.435 (9)				

Bond Angles (deg)

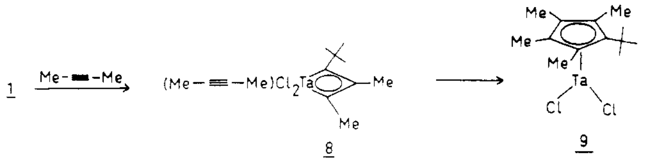
Cl(1)–Ta–Cl(2)	80.4 (1)	Cl(1)–Ta–C(1)	77.8 (2)	C(4)–C(3)–C(8)	122.8 (5)	C(7)–C(3)–C(8)	129.5 (5)
Cl(2)–Ta–C(1)	128.3 (2)	Cl(1)–Ta–H(1a)	76.0 (20)	Ta–C(4)–C(3)	72.1 (3)	Ta–C(4)–C(5)	73.0 (3)
Cl(2)–Ta–H(1a)	150.3 (20)	C(1)–Ta–H(1a)	28.3 (20)	C(3)–C(4)–C(5)	108.2 (5)	Ta–C(4–)C(16)	124.5 (4)
Cl(1)–Ta–C(2)	80.7 (2)	Cl(2)–Ta–C(2)	113.3 (2)	C(3)–C(4)–C(16)	127.0 (6)	C(5)–C(4)–C(16)	124.6 (5)
C(1)–Ta–C(2)	108.6 (2)	H(1a)–Ta–C(2)	80.5 (20)	Ta–C(5)–C(4)	73.3 (3)	Ta–C(5)–C(6)	76.6 (3)
Cl(1)–Ta–C(3)	147.2 (1)	Cl(2)–Ta–C(3)	115.3 (1)	C(4–)C(5)–C(6)	108.1 (5)	Ta–C(5)–C(12)	114.9 (4)
C(1)–Ta–C(3)	69.9 (2)	H(1a)–Ta–C(3)	78.2 (19)	C(4)–C(5)–C(12)	124.4 (5)	C(6)–C(5)–C(12)	127.5 (6)
C(2)–Ta–C(3)	114.6 (2)	Cl(1)–Ta–C(4)	146.5 (1)	Ta–C(6)–C(5)	70.3 (3)	Ta–C(6)–C(7)	71.7 (3)
Cl(2)–Ta–C(4)	132.7 (1)	C(1)–Ta–C(4)	82.3 (2)	C(5)–C(6)–C(7)	108.6 (5)	Ta–C(6)–C(21)	126.1 (4)
H(1a)–Ta–C(4)	73.7 (20)	C(2)–Ta–C(4)	80.5 (2)	C(5)–C(6)–C(21)	121.4 (5)	C(7)–C(6)–C(21)	129.9 (5)
C(3)–Ta–C(4)	34.2 (2)	Cl(1)–Ta–C(5)	150.2 (1)	Ta–C(7)–C(3)	70.8 (3)	Ta–C(7)–C(6)	75.1 (3)
Cl(2)–Ta–C(4)	106.0 (2)	C(1)–Ta–C(5)	115.9 (2)	C(3)–C(7)–C(6)	107.0 (5)	Ta–C(7)–C(26)	126.4 (4)
H(1a)–Ta–C(5)	103.4 (20)	C(2)–Ta–C(5)	70.0 (2)	C(3)–C(7)–C(26)	121.9 (5)	C(6)–C(7)–C(26)	130.4 (5)
C(3)–Ta–C(5)	56.6 (2)	C(4)–Ta–C(5)	33.7 (2)	C(3)–C(8)–C(9)	113.2 (5)	C(1)–C(9)–C(8)	108.3 (5)
Cl(1)–Ta–C(6)	155.4 (1)	Cl(2)–Ta–C(6)	78.0 (1)	C(1)–C(9)–C(10)	108.9 (5)	C(8)–C(9)–C(10)	112.0 (5)
C(1)–Ta–C(6)	125.3 (2)	H(1a)–Ta–C(6)	128.1 (20)	C(1)–C(9)–C(11)	110.8 (5)	C(8)–C(9)–C(11)	111.7 (5)
C(2)–Ta–C(6)	97.1 (2)	C(3)–Ta–C(6)	55.6 (2)	C(10)–C(9)C(11)	105.0 (5)	C(5)–C(12)–C(13)	111.8 (5)
C(4)–Ta–C(6)	55.0 (2)	C(5)–Ta–C(6)	33.2 (2)	C(2)–C(13)–C(12)	108.8 (5)	C(2)–C(13)–C(14)	109.1 (5)
Cl(1)–Ta–C(7)	152.5 (1)	Cl(2)–Ta–C(7)	82.3 (1)	C(12)–C(13)–C(14)	111.5 (5)	C(2)–C(13)–C(15)	110.5 (5)
C(1)–Ta–C(7)	96.6 (2)	H(1a)–Ta–C(7)	111.6 (19)	C(12)–C(13)–C(15)	109.3 (5)	C(14)–C(13)–C(15)	107.6 (5)
C(2)–Ta–C(7)	126.1 (2)	C(3)–Ta–C(7)	34.1 (2)	C(4)–C(16)–C(17)	117.2 (5)	C(16)–C(17)–C(18)	112.3 (6)
C(4)–Ta–C(7)	56.2 (2)	C(5)–Ta–C(7)	56.1 (2)	C(16)–C(17)–C(19)	112.1 (6)	C(18)–C(17)–C(19)	107.9 (6)
C(6)–Ta–C(7)	33.2 (2)	Ta–C(1)–H(1a)	82.1 (40)	C(16)–C(17)–C(20)	107.1 (6)	C(18)–C(17)–C(20)	108.4 (6)
Ta–C(1)–H(1b)	115.0 (40)	H(1a)–C(1)–H(1b)	108.1 (55)	C(19)–C(17)–C(20)	109.0 (6)	C(6)–C(21)–C(22)	115.7 (5)
Ta–C(1)–C(9)	128.6 (4)	H(1a)–C(1)–C(9)	113.7 (41)	C(21)–C(22)–C(23)	113.2 (7)	C(21)–C(22)–C(24)	109.8 (6)
H(1b)–C(1)–C(9)	106.0 (40)	Ta–H(1a)–C(1)	69.6 (39)	C(23)–C(22)–C(24)	108.0 (9)	C(21)–C(22)–C(25)	110.7 (6)
Ta–C(2)–H(2a)	103.2 (25)	Ta–C(2)–H(2b)	108.8 (28)	C(23)–C(22)–C(25)	110.3 (10)	C(24)–C(22)–C(25)	104.5 (7)
H(2a)–C(2)–H(2b)	100.8 (37)	Ta–C(2)–C(13)	118.2 (4)	C(7)–C(26)–C(27)	115.1 (5)	C(7)–C(26)–C(28)	111.9 (5)
H(2a)–C(2)–C(13)	111.7 (27)	H(2b)–C(2)–C(13)	112.4 (28)	C(27)–C(26)–C(28)	105.8 (6)	C(7)–C(26)–C(29)	107.5 (5)
Ta–C(3)–C(4)	73.7 (3)	Ta–C(3)–C(7)	75.1 (3)	C(27)–C(26)–C(29)	105.8 (5)	C(28)–C(26)–C(29)	110.5 (6)
C(4)–C(3)–C(7)	107.7 (5)	Ta–C(3)–C(8)	118.1 (4)				

Table V. Torsion Angles (deg) in 7

Ta–C(1)–C(9)–C(8)	−8.1 (8)
C(3)–C(8)–C(9)–C(1)	−4.0 (7)
Ta–C(2)–C(13)–C(12)	47.2 (6)
C(5)–C(12)–C(13)–C(2)	−27.2 (7)
Ta–C(3)–C(8)–C(9)	12.6 (7)
C(1)–Ta–C(3)–C(8)	−12.4 (5)
C(3)–Ta–C(1)–C(9)	11.2 (6)
Ta–C(5)–C(12)–C(13)	0.8 (6)
C(2)–Ta–C(5)–C(12)	17.4 (4)
C(5)–Ta–C(2)–C(13)	−35.1 (5)
H(1a)–Ta–C(2)–C(13)	−143 (2)
H(1a)–Ta–C(2)–H(2a)	93 (4)
H(1a)–Ta–C(2)–H(2b)	−13 (4)
H(1a)–C(1)–Ta–C(2)	7 (4)

Thus Cl(1) lies approximately opposite the centroid of the Cp ring (Cp–Ta–Cl(1) = 175.9 (1)°, where Cp denotes the ring centroid), and Cl(2), C(1), and C2) lie in a plane parallel to this ring, the Cp centroid–Ta–C(1), –C(2), and –Cl(2) angles being 98.8 (2)°, 98.2 (2)°, and 103.5 (1)°, respectively.[13] It is noticeable that the "axial" Cl(1)–Ta distance is longer than the "equatorial" Cl(2)–Ta length (2.454 (2) vs. 2.362 (2) Å).[14] The axial Cl(1) to equatorial ligand angles are approximately constant (C(1)–Ta–Cl(1) = 77.8 (2)°, C(2)–Ta–Cl (1) = 80.7 (2)°, and Cl(1)–Ta–Cl(2) = 80.4 (1)°) as is appropriate for the 3.3.1 description of 7.

Scheme II



There exists an additional valence interaction between the tantalum atom and the electrons of a C–H bond (C(1)H(1a)), allowing some relief of electronic unsaturation. This interaction (Ta–H(1a) = 2.30 (8) Å) causes a marked distortion in the geometry around C(1), the Ta–C(1)–H(1a) angle is substantially reduced from the regular tetrahedral value at 82 (4)°, and correspondingly the Ta–C(1)–C(9) angle is enlarged to 128.6 (4)°. In contrast, the geometry

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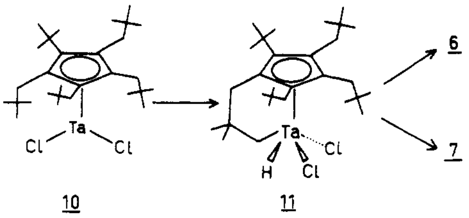
[13] The Cp centroid–Ta–C(1), –C(2) and –Cl(1) angles are rather smaller than those predicted[12] for the 3.3.1 structure in the model compound $V(\eta^5\text{-}C_5H_5)H_4^{4-}$ (112°); this is presumably because of the greatly increased bulk of Cl^- (the axial ligand in 7) and the equatorial ligands here as compared with H^- in the model.

[14] An interesting comparison may be made with the 3.4.1 structure adopted by a $CpTaL_5$ complex $Ta(\eta^5\text{-}C_5H_5)(CO)Cl_2(PMe_3)_2$.[15] In this complex the axial Ta–Cl bond length is even longer than in 7 (2.518 (4) Å, cf. Ta–Cl_{eq} = 2.539 (4) Å) and Cp–Ta–L_{eq} angles average 103.8°.

[15] Burt, R. J.; Leigh, G. J.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 793.

Scheme III



at C(2) is more orthodox, angles being much closer to the regular tetrahedral values Ta–C(2)–C(13) = 118.2 (4)°, other angles between 101 (4) and 112 (3)°.

Discussion

We propose that the products **2a** and **3a** obtained in the reaction of the tantalum alkylidyne complex **1** with 2-butyne, neat and in dichloromethane respectively, are formed via the intermediacy of a tantalacyclobutadiene complex $[(MeC{\equiv}CMe)TaCl_2\{C(t\text{-}Bu)C(Me)C(Me)\}]$, **8**, and a cyclopentadienyltantalum dichloride, $[(\eta^5\text{-}C_5(t\text{-}Bu)(Me)_4)TaCl_2]$, **9** (cf. Scheme II).

Such intermediates have been postulated by Schrock et al.[16] to explain the formation of the related tungsten complexes $[(\eta^5\text{-}C_5(t\text{-}Bu)(Me)_4)WCl_4]_2$ and $[(\eta^5\text{-}C_5(t\text{-}Bu)(Me)_4)WCl_2(MeC{\equiv}CMe)]$ from the reaction of $[W(CCMe_3)(MeOCH_2CH_2OMe)Cl_3]$ with excess 2-butyne. In fact, they were able to isolate the metallacyclobutadiene from the reaction of $[W(CCMe_3)(MeOCH_2CH_2OMe)Cl_3]$ with 1 equiv of 2-butyne. When we react **1** with less than 4 equiv of alkyne, we invariably observe the formation of mixtures of the cyclopentadienyl complexes and starting material and no tantalacyclobutadiene species are detected. Evidence that the Cp ligand formation proceeds nevertheless via such an intermediate is obtained from the reaction of **1** with the bulky bis(trimethylsilyl)acetylene, which results in formation of the tantalacyclobutadiene complex $[(Me_3SiC{\equiv}CSiMe_3)TaCl_2\{C(t\text{-}Bu)C(SiMe_3)C(SiMe_3)\}]$, **5**. Collapse of the tantalacyclobutadiene complex **8** is then proposed to give the cyclopentadienyl complex **9**, which in 2-butyne is scavenged by a solvent molecule to give the Ta(III) acetylene adduct **2a**, whereas in dichloromethane solution it is oxidized by the solvent to give the Ta(V) tetrachloride **3a**.

The early stage of the formation of the reaction products of **1** with dineopentylacetylene parallels the reaction with other acetylenes to the point where the 12-valence electron species $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_4)TaCl_2]$, **10**, is formed (cf. Scheme III). This species is apparently capable of activating a C–H bond of one of the neopentyl substituents on the cyclopentadienyl ring.[17] In our opinion two factors can be held responsible for the efficiency of this reaction (formation of $[(\eta^5\text{-}C_5(CH_2CMe_3)_4(t\text{-}Bu))TaCl_4]$ is not observed even in dichloromethane–carbon tetrachloride): (i) The *gem*-dimethyl substitution of the neopentyl group, which is known[18] to reduce both the number of extra gauche interactions and the loss of internal rotational freedom upon cyclization of the alkyl group. (ii) The mutual steric hindrance of the four neopentyl groups and the *tert*-butyl group on the cyclopentadienyl ligand. Inspection of space-filling models of the cyclopentadienyl ligand reveals that one of the two neopentyl groups next to the *t*-butyl group is strongly bent toward the metal, and we believe that this greatly enhances the rate of C–H bond activation in our system. The tantalum hydride intermediate **11**, which is probably formed in the first C–H activation is not observed. It either gets involved in a second metalation of a neopentyl substituent to give **7** or is converted—in chlorinated solvents—to the trichloro complex **6**. Interestingly, the second C–H activation and the concomitant loss of hydrogen[19] can no longer be described as an oxidative addition/reductive elimination sequence, **11** being a d° system, and the reaction probably proceeds via the four-center mechanism which has been proposed for similar reactions in other d° system.[20] A related interaction between a d° metal center and a nonactivated C–H bond is observed in **7**; it is clearly indicated by the crystal structure and its NMR spectroscopic properties. Thus, in the ^1H NMR spectrum H(1a) (δ 0.33) and H(1b) (δ 4.03) show a large difference in chemical shift, in contrast to the H(2a) and H(2b) resonances, which have similar shifts (δ 2.01 and 2.50). This is consistent with H(1a) approaching a bridging C–H–Ta site, and therefore a high field chemical shift, while H(1b) moves to a lower field shift as C(1) becomes more carbenoid in nature.

The structural information obtained from the crystal structure data indicates a substantial distortion at C(1) toward a state where H(1a) is partly attached to the metal and C(1) is partly carbenoid, hence the short Ta–H(1a) distance, small Ta–C(1)–H(1a) angle, and increased Ta–C(1)–C(9) angle noted above. In addition, the Ta—C(1) length is significantly shorter than Ta—C(2) (2.176 (7) vs. 2.215 (6) Å), the latter being the usual range for Ta(V)—alkyl single bonds,[21] whereas full Ta=C double bonds are rather shorter than Ta—C(1).[22] This internal calibration indicates a Ta–C(1) bond order marginally greater than unity. The increased Ta–H(1a) and Ta–C(1) bond orders (and presumably reduced C(1)–H(1a) bond order, although this is not directly observable from X-ray data) parallel those crystallographically characterized in a number of *alkylidene* complexes[23] but are now for the first time observed for a tantalum(V) *alkyl* complex.

A methyl ligand which shows an even larger $M\text{–}C_\alpha\text{–}H$ angle distortion than that in **7** has been characterized by Green and co-workers in a 12-electron d° titanium complex $[Ti(Cl)_3(Me_2PCH_2CH_2PMe_2)(Me)]$.[24] This shows $Ti\text{–}C_\alpha\text{–}H$ = 70 (2)°, Ti–H = 2.03 (4) Å, and $Ti\text{–}C_\alpha$ = 2.149 (5) Å. This last $M\text{–}C_\alpha$ bond length shows a similar decrease (ca. 0.05 Å) relative to a single metal–alkyl bond (cf. $Ti\text{–}C_\alpha$ = 2.211 (5) Å in $Ti(\eta^7\text{-}C_7H_7)(Me_2PCH_2CH_2PMe_2)(C_2H_5)$,[25] as does **7**.

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[16] Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wassermann, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808.

[17] Up till now only one example has been reported of a δ-hydrogen activation in a η^5-cyclopentadienyl complex: $[\{\eta^5\text{-}C_5Me_4(CH_2CMe_3)\}_2ZrH_2]$ evolves hydrogen at 25 °C followed by oxidative addition of a γ-C–H bond of the neopentyl group to the metal center. McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.

[18] Shaw, B. L. *J. Organomet. Chem.* **1980**, *200*, 307.

[19] The evolution of hydrogen was confirmed in a separate experiment (cf. Experimental Section).

[20] Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

[21] $Ta\text{–}CH_3$ in $[Ta(\eta^5\text{-}C_5H_5)_2(CH_2)(CH_3)]$ is 2.246 (12) Å; see ref 1a. $Ta\text{–}CH_2C_6H_5$ in $[Ta(\eta^5\text{-}C_5Me_5)(CH_2C_6H_5)_2(CHC_6H_5)]$ is 2.188 (15) and 2.233 (14) Å. Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744. $Ta\text{–}CH_2R$ in $[Ta(\eta^5\text{-}C_5Me_5)(CH_2CH_2CH_2CH_2)Cl_2]$ is 2.217 (8) Å. Churchill, M. R.; Youngs, W. R. *Inorg. Chem.* **1980**, *19*, 3106.

[22] $Ta{=}CH_2$ in $[Ta(\eta^5\text{-}C_5H_5)_2(CH_2)(CH_3)]$ is 2.026 (10) Å; see ref 1a. $Ta{=}CHCMe_3$ in $[Ta(\eta^5\text{-}C_5H_5)_2Cl(CHCMe_3)]$ is 2.030 (6) Å. Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *7*, 1957.

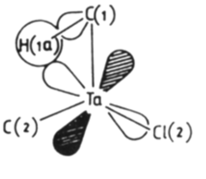
[23] The most precisely (neutron data) determined of these $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ and $[Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)]$ show, respectively, Ta–H distances which are 2.119 (4) and 2.045 (5) Å, Ta–C–H angles of 84.8 (2) and 78.1 (3)°, and short Ta–C distances of 1.898 (2) and 1.946 (3) Å (cf. $Ta{=}CH_2$ in $[Ta(\eta^5\text{-}C_5H_5)_2(CH_2)(CH_3)]$, 2.026 (10) Å; see ref 1a. Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.

[24] Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1410.[29]

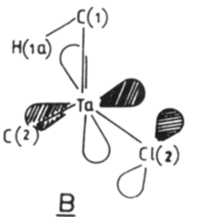
[25] Green, M. L. H.; Hazel, N. J.; Gebruik, P. D.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1983**, 356.

The geometry of the Ta–C(1)–H(1a) interaction is such that H(1a) lies very close to the plane of C(1), C(2), and Cl(2) (hence Cp–Ta–H(1a) = 100 (2)°) and between C(1) and C(2).

The orientation adopted by H(1a) allows interaction of the C(1)–H(1a) bond electrons with one of the lowest lying pair of unoccupied d orbitals on Ta (d_{xy} and $d_{x^2-y^2}$, see ref 12) which lie approximately parallel to the Cp ring. The other of the pair is then presumably able to accommodate a degree of π-donation from the equatorial chloride ligand Cl(2); these two interactions are depicted schematically below (A and B, respectively). This favorable interaction may also account for some of the relative shortness of Ta–Cl(2) vs. Ta–Cl(1).



A



B

The orientation of H(1a) models the appropriate geometry for the α-abstraction reaction in its early stages. Thus, C(1) and C(2) are mutually cis (kinetic evidence suggests that alkyl ligands in $CpTaX_2(alkyl)_2$ must be cis to undergo α-abstraction[26]) and H(1a) lies nearly in the Ta, C(1), C(2) plane (torsion angle C(2)–Ta–C(1a)–H(1a) = 7 (4)°). The C(2)···H(1a) distance is rather long (2.92 (8) Å), indicating that the α-abstraction "reaction" is halted early in **7**. A variety of factors may prevent full α-abstraction in **7**; ring conformation effects in the C(2), Ta, C(5), C(12), C(13) and C(1), Ta, C(3), C(8), C(9) rings may inhibit the geometry variations required to "pass" H(1a) across from C(1) to C(2) (see, e.g., those suggested in ref 27) and/or the end product $[(\eta^5\text{-}C_5(CH_2CMe_3)_3(t\text{-}Bu)(CH_2CMe_2\underbrace{CH))Ta}Cl_2]$ may be too congested for stability.

The effects of the coordination of the C(1)–H(1a) bond to Ta on the dihedral angles in the Ta–C(1)–C(9)–C(8)–C(3) ring are marked (see Table V), with this ring being much flattened (|angles| < 12.6 (7)°, cf. for C(2) ring |angles| < 47.2 (6)°) in order to bring H(1a) in to the electronically required orientation (A). As noted above this ring conformation also moves C(10) away from C(28) as required to minimize unfavorable steric interactions. Thus the steric bulk of the *tert*-butyl Cp substituent dictates that the metalated neopentyl group adjacent to it must be the one which has the C_α–H valence interaction. The unusual 3.3.1 geometry of **7** greatly facilitates the above coordinative interaction of the C(1)–H(1a) bond with the metal center, which would, in fact, be difficult—if possible at all—in the preferred 3.4 geometry of $CpML_4$ type molecules.

A recent theoretical treatment of d^4 $CpML_4$ molecules has analyzed the reasons for their preference for the "four-legged piano-stool" geometry.[12] Two principal factors seem to favor the 3.4 geometry: first the stabilization of a metal d orbital (*xy* in the notation of ref 12) occupied in the d^4 case and, second, steric pressure on the axial site of the 3.3.1 structure which render it unstable. In **7** the first of these poses no problem, since this is a d° species and hence the important metal orbital is unoccupied. The steric demands of the ligands in **7** undoubtedly play a major role, but perhaps in the opposite sense to that indicated in ref 12, by increasing the nonbonded repulsions in the basal plane of the 3.4 structure to energetically unacceptable levels.

Experimental

General Procedures. All experiments were performed in an inert atmosphere in rigorously dried solvents. Spectroscopic measurements were carried out with the following instrumentation: ^1H NMR, Bruker WH-90; ^{13}C NMR, Bruker WM-250; mass spectra, Finnigar TSQ mass spectrometer.

Materials. The preparation of $[\{Cl_2(DME)Ta(\mu\text{-}CCMe_3)\}_2Zn(\mu\text{-}Cl)_2]$, **1**, has been described previously.[2] All acetylenes were commercially available, except 2,2,5,5-tetramethyl-3-hexyne and 2,2,7,7-tetramethyl-4-octyne, which were prepared as described in ref 28.

Preparation of $[(\eta^5\text{-}C_5Me_4(t\text{-}Bu))TaCl_2(MeC{\equiv}CMe)]$, 2a. A suspension of **1** (0.87 g, 0.908 mmol) in 2-butyne (25 mL) was stirred for 24 h at room temperature. Excess butyne was removed in vacuo, the residue dissolved in toluene, and the solution filtered. The solvent was removed in vacuo to give the crude product which was purified by recrystallization from toluene–hexane (yield 80%). Anal. Calcd for $C_{17}H_{27}Cl_2Ta$: C, 42.25; H, 5.63; Cl, 14.67. Found: C, 42.08; H, 5.50; Cl, 14.86.

Preparation of $[(\eta^5\text{-}C_5H_2(t\text{-}Bu)_3)TaCl_2(t\text{-}BuC{\equiv}CH)]$, 2d. This compound was prepared from **1** (1 mmol) and 3,3-dimethyl-1-butyne (8 mmol) in a procedure analogous to that described for **7** (recrystallized from hexane; yield 82%). Anal. Calcd for $C_{23}H_{39}Cl_2Ta$: C, 48.69; H, 6.93; Cl, 12.50. Found: C, 48.67; H, 6.99; Cl, 12.40.

Preparation of $[(\eta^5\text{-}C_5Me_4(t\text{-}Bu))TaCl_4]$, 3a. To a red solution of **1** (0.87 g, 0.908 mmol) in CH_2Cl_2 (25 mL) was added 2-butyne (0.24 g, 4.4 mmol). The reaction mixture was stirred at room temperature for 3 h, by which time the color had changed from red to yellow-brown. The solvent and excess butyne were removed in vacuo, the residue was dissolved in toluene, and the solution filtered. The solvent was removed in vacuo to give the crude product which was purified by recrystallization from toluene–hexane (yield 70%). Anal. Calcd for $C_{13}H_{21}Cl_4Ta$: C, 31.22; H, 4.23. Found: C, 31.41; H, 4.37.

Preparation of $[(\eta^5\text{-}C_5Et_4(t\text{-}Bu))TaCl_4]$, 3b. This compound was prepared from **1** and 3-hexyne in a procedure analogous to that described for **3a** (recrystallized from hexane; yield 65%). Anal. Calcd for $C_{17}H_{29}Cl_4Ta$: C, 36.71; H, 5.26; Cl, 25.50. Found: C, 36.53; H, 5.28; Cl, 25.45.

Preparation of $[(\eta^5\text{-}C_5(n\text{-}Pr)_4(t\text{-}Bu))TaCl_4]$, 3c. This compound was prepared from **1** and 4-octyne in a procedure analogous to that described for **3a** (recrystallized from hexane; yield 67%). Anal. Calcd for $C_{21}H_{37}Cl_4Ta$: C, 41.20; H, 6.09; Cl, 23.16. Found: C, 41.11; H, 6.03; Cl, 23.00.

Preparation of $[(\eta^5\text{-}C_5H_2(t\text{-}Bu)_3)TaCl_4]$, 3d. This compound was prepared from **1** and 3,3-dimethyl-1-butyne in a procedure analogous to that described for **3a**. As a solvent a mixture of CH_2Cl_2 (12.5 mL) and CCl_4 (12.5 mL) was used (recrystallized from hexane; yield 75%). Anal. Calcd for $C_{17}H_{29}Cl_4Ta$: C, 36.71; H, 5.26; Cl, 25.50. Found: C, 36.48; H, 5.22; Cl, 25.26.

Preparation of $[(\eta^5\text{-}C_5H_2(i\text{-}Bu)_2(t\text{-}Bu))TaCl_4]$, 3e. This compound was prepared from **1** and 4-methyl-1-pentyne in a procedure analogous to that described for **3d**. The yield of the mixture (see text) of **3e′** and **3e″** was 67% after recrystallization from hexane.

Reaction of 1 with 2,2,7,7-Tetramethyl-4-octyne in CH_2Cl_2. In a procedure analogous to the preparation of **3a**, **1** was reacted with dineopentylacetylene for 24 h to give an orange solution. After removal of the solvent in vacuo, the residue was taken up in hexane and filtered. This solution deposited red **6** which contained (NMR) minor amounts of **7**. The remaining solution

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was reduced in vacuo, and the resulting oil was crystallized with diethyl ether to give yellow **7**, in 63% yield. Inspection of the ^{1}H NMR spectrum of the initial reaction mixture revealed that **6** and **7** were formed in a 1:10 ratio.

Preparation of $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_2(CH_2C(Me)_2\overline{CH_2})_2)TaCl_2]$, 7. Solid **1** (1.0 g, 1.04 mmol) was covered with toluene (5 mL) and rapidly stirred. To this mixture was slowly added dineopentylacetylene (0.694 g, 4.18 mmol) and THF (0.31 g, 4.3 mmol) in toluene (5 mL). The reaction mixture was stirred for 3 h at room temperature. The solvent was removed in vacuo, the residue dissolved in hexane, and the solution filtered. The clear solution was reduced and deposited yellow **7** (0.87 g, 70%) on cooling. Anal. Calcd for $C_{29}H_{51}Cl_2Ta$: C, 53.46; H, 7.89; Cl, 10.88. Found: C, 53.39; H, 7.80; Cl, 10.90.

Analysis of the Volatiles Evolved in the Formation of 7. The above reaction was repeated with 0.300 g (0.335 mmol) of **1** in a closed vessel. The reaction was stirred for 3 h after which the vessel was depressurized. An amount of ca. 12 mL of gaseous products (corresponding to ca. 0.53 mmol) was collected, and GC analysis showed this to contain 10% H_2, the remainder being N_2 and Ar (the volume in the vessel above the liquids amounted to ca. 100 mL and contained an atmosphere of N_2 and Ar). The recovery of H_2 thus amounted to ca. 80%.

Reaction of 1 with Bis(trimethylsilyl)acetylene. In a procedure analogous to that described for the preparation of **3a**, **1** was reacted with bis(trimethylsilyl)acetylene. The resulting brown oil could not be crystallized and contained traces of starting acetylene. Spectroscopic data for **5** refer to this impure product.

Reaction of 1 with 3,3-Dimethyl-1-butyne in CH_2Cl_2. The procedure followed was that described for the preparation of **3a**. Thus, **1** was reacted with 3,3-dimethyl-1-butyne, and after workup there remained a solid product mixture from which a small sample of impure **4** (containing ~5% **3d** by ^{1}H-NMR) was obtained by extraction with hexane. Spectroscopic data of **4** refer to this impure product.

Crystal Structure Determination of $[(\eta^5\text{-}C_5(t\text{-}Bu)(CH_2CMe_3)_2(CH_2CMe_2\overline{CH_2})_2TaCl_2]$, 7

Crystal data: $C_{29}H_{51}Cl_2Ta$, $M = 651.6$, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.197$ (5) Å, $b = 17.276$ (5) Å, $c = 11.273$ (3) Å, $\beta = 90.74$ (3)°, $U = 2959.4$ (1.5) Å^3, $Z = 4$, $D_{\text{calcd}} = 1.46$ g·cm^{-3}, graphite monochromated, Mo Kα, X radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 38.7 cm^{-1}.

A small (ca. 0.2 × 0.3 × 0.7 mm) single crystal of **7** was mounted under N_2 in a thin-walled glass capillary, using silicone grease as adhesive, for X-ray study. All diffraction measurements were made at 220 K on a Nicolet *P*3*m* diffractometer. A total of 3438 diffracted intensities were measured in a unique quadrant of reciprocal space in the range $4 < 2\theta < 40°$. Two check reflections remeasured after every 50 data showed no significant fluctuation or decay during the experiment. The intensity data were corrected for absorption on the basis of an empirical six-parameter fit to 365 azimuthal scan data, transmission coefficients varied between 0.134 and 0.080. After deletion of duplicate measurements and systematic absences and averaging of symmetry related structure factors, 2773 data remained; of these 2423 with $I > 2\sigma(I)$ were used in structure solution and refinement. The structure was solved by conventional heavy-atom methods (Patterson and Fourier) and all hydrogen atoms (barring some on C(23), C(24), and C(25)) were located directly. All non-hydrogen atoms were assigned anisotropic vibrational parameters; H(1a), H(1b), H(2a), and H(2b) were refined with isotropic vibrational parameters and without constraints, other hydrogens being assigned idealized geometrics and fixed isotropic vibrational parameters. Refinement by blocked-cascade full-matrix least squares leads to final residuals $R = 0.026$, $R' = 0.031$, and $S = 1.233$ with weights $w = [\sigma^2(F_o) + 0.0002F^2]^{-1}$, where $\sigma^2(F_o)$ is the variance in F_o estimated from counting statistics alone. $[R = \sum||F_o| - |F_c||/\sum|F_o|$; $R' = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; $S = [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.] A final differences electron density synthesis showed no features >0.59 e Å^{-3}, or < −0.67 e Å^{-3}, with the largest being in regions of no chemical significance. Tables VII–IX, listing the anisotropic vibrational parameters, fixed hydrogen atom parameters, and observed and calculated structure factors, have been deposited in the microfilm edition of the journal. Table VI lists the atomic positional and effective isotropic vibrational parameters for the non-hydrogen atoms and H(1a), H(1b), H(2a), and H(2b). All crystallographic calculations were carried out on an in-house Data General ECLIPSE mini-computer using programs of the SHELXTL package.

Supplementary Material Available: Tables of coordinates and isotropic thermal parameters, anisotropic temperature factors, hydrogen coordinates and isotropic thermal parameters, and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.