Organometallics 1987, *6*, 73–80

Synthesis and Spectroscopic Properties of Tantalum μ-Alkylidyne Compounds Containing Bulky Aryloxide Ligands: X-ray Structures of the Asymmetric Derivatives $(Me_2SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)(OAr\text{-}2,6\text{-}Ph_2)$ and $(Me_2SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2$ ($OAr\text{-}2,6\text{-}Ph_2$ = 2,6-Diphenylphenoxide; $OAr\text{-}2,6\text{-}t\text{-}Bu_2$ = 2,6-Di-*tert*-butylphenoxide)[1]

Phillip E. Fanwick, Ann E. Ogilvy, and Ian P. Rothwell*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received June 6, 1986

The reaction of the mixed alkyl–alkylidyne compound $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)]_2$ (1) with a series of 2,6-disubstituted phenols has been investigated. 2,6-Dimethylphenol ($HOAr\text{-}2,6\text{-}Me_2$) reacts with 1 to eventually produce the known $Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_5$ via a number of unidentified intermediates. With the more bulky 2,6-diphenylphenol ($HOAr\text{-}2,6\text{-}Ph_2$) reaction proceeds by sequential loss of Me_4Si to yield red mono- and disubstituted complexes 2 and 3 and to eventually give the green, tetrasubstituted derivative $[(Ph_2\text{-}2,6\text{-}ArO)_2Ta(\mu\text{-}CSiMe_3)_2]_2$ (4). Spectroscopic data on the disubstituted derivatives 3 is consistent with the presence of all three of the substitutional isomers possible for molecules with pseudotetrahedral geometry about the two tantalum metal atom centers. The 1,1-substitution and syn and anti forms of the 1,2-substitution isomers were present in essentially identical amounts. In contrast the use of 2,6-di-*tert*-butylphenol ($HOAr\text{-}2,6\text{-}t\text{-}Bu_2$) was found to lead to only one of the possible disubstituted product isomers 5. Structural studies showed 5 to in fact be the 1,1-substituted isomer $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2]$. Both of the asymmetric derivatives 2 and 5 have been subjected to a single-crystal X-ray diffraction study. Both retain the initial dimetallocyclobutadiene $Ta_2(\mu\text{-}CSiMe_3)_2$ core with the terminal alkyl- and aryloxide donor atoms arranged in a pseudotetrahedral arrangement about each tantalum atom. The Ta–Ta distances of 2.8825 (6) and 2.9071 (4) Å for 2 and 5 are consistent with no metal–metal bond being present as expected for these d^0–d^0 dinuclear species. Crystal data for $Ta_2Si_5OC_{38}H_{64}$ (2) at 23 °C are $a = 10.343$ (1) Å, $b = 12.209$ (2) Å, $c = 37.411$ (6) Å, $\beta = 84.23$ (1)°, $Z = 4$, and $d_{calcd} = 1.469$ g cm^{-3} in space group $P2_1/n$. Of the 8690 unique data collected with Mo Kα, the 4597 with $I > 3.0\sigma(I)$ were used in the least-squares refinement to give $R = 0.042$ and $R_w = 0.056$. Crystal data for $Ta_2Si_4O_2C_{44}H_{82}$ at −160 °C are $a = 12.283$ (6) Å, $b = 23.692$ (6) Å, $c = 17.205$ (6) Å, $Z = 4$, and $d_{calcd} = 1.482$ g cm^{-3} in space group *Pbcn*. Of the 7306 unique data collected with Mo Kα, the 4118 with $I > 3.0\sigma(I)$ were used in the least-squares refinement to give $R = 0.038$ and $R_w = 0.056$. The bis(phenoxide) 5 will undergo thermolysis to generate the known bis-cyclometalated derivative $Ta(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)_2(CH_2SiMe_3)$ ($OC_6H_3\text{-}t\text{-}BuCMe_2CH_2$ = cyclometalated 2,6-di-*tert*-butylphenoxide), but only in very low yield.

Introduction

During our studies of the early-transition-metal organometallic chemistry associated with bulky 2,6-dialkylphenoxide ligands,[1-3] we have characterized the sometimes mild intramolecular activation of the aliphatic carbon–hydrogen bonds of 2,6-di-*tert*-butylphenoxide.[4] The reaction typically involves d^0 metal centers with alkyl leaving groups to generate a stable six-membered metallacycle. For Ta(V) we demonstrated that the intramolecular metalation of these groups can be achieved both with alkylidene ($M{=}CR_2$) as well as alkyl functional groups.[5] The former reaction involves the intramolecular addition of the aliphatic CH bond to the tantalum–carbon double bond, and we have found that the reaction is enthalpically favored over the corresponding reaction with alkyl leaving groups.[5] The early-transition-metal alkylidyne ($M{\equiv}C{-}R$) function would on the basis of these results be expected to perhaps be an even more potent function for activating the CH bonds in this ligand. This idea is given support by the observation by Schrock et al. that attempts to prepare a tungsten alkylidyne from $W(CCMe_3)Cl_3(dme)$ and $LiOAr\text{-}2,6\text{-}t\text{-}Bu_2$ led only to the isolation of the cyclometalated alkylidene $W(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)(OAr\text{-}2,6\text{-}t\text{-}Bu_2)(CH\text{-}t\text{-}Bu)Cl$.[6] Our attempts to isolate tantalum alkylidyne complexes containing 2,6-di-*tert*-butylphenoxide has led us to investigate the reactions of the known, dimeric $[(Me_2SiMe_3)_2Ta(\mu\text{-}CSiMe_3)]_2$[7] (1) with phenolic reagents. Chisholm and workers have shown that the reaction of the related tungsten–tungsten single bonded $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$[8] with alcohols leads to the initial stepwise replacement of the terminal alkyl groups leaving the central 1,3-ditungstacyclo-

---

[1] The Chemistry of Sterically Crowded Aryloxide Ligands. 6. For part 5, see: Latesky, S. L.; McMullen, A. K., Keddington, J.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995.

[2] (a) Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575. (b) McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1072. (c) Durfee, L. D.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 4569.

[3] (a) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906. (b) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1249. (c) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 1643.

[4] (a) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (b) Chamberlain, L. R.; Keddington, J.; Huffman, J. C.; Rothwell, I. P. *Organometallics* **1982**, *1*, 1538. (c) Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1984**, *106*, 1847. (d) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981.

[5] Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502.

[6] Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554.

[7] (a) Huq, F.; Mowat, W.; Skapski, A. C.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1971**, 144. (b) Anderson, R. A.; Gayler, A. L.; Wilkinson, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 609.

[8] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 696.

0276-7333/87/2306-0073$01.50/0

Table I. Selected ^1H and ^{13}C NMR Data[a]

	^1H		^{13}C		
compd	$\delta(CH_2SiMe_3)$	$\delta(SiMe_3)$	$\delta(\mu\text{-}CSiMe_3)$	$\delta(CH_2SiMe_3)$	$\delta(SiMe_3)$
$[Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)]_2$ (1)[c]	1.00	0.20 (μ)	404.7	76.8	3.7
		0.46			5.0
$[Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr\text{-}2,6\text{-}Ph_2)(CH_2SiMe_3)]$ (2)	0.03	−0.10 (μ)	399.3	64.7	3.35
	0.90	0.16		78.3	3.4
	1.23	0.34		79.8	3.8
		0.41			4.7
$[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_2(OAr\text{-}2,6\text{-}Ph_2)_2]$ (3) (three isomers)	0.92	−0.45	391.4	63.5	1.8
	0.51	−0.32	387.7	64.2	2.3
	b	−0.19	385.2	74.4	2.6
		0.25			3.1
		0.26			3.2
		0.45			*b*
$[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2]$ (5)	1.22	0.22 (μ)	386.3	77.3	3.7
		0.40			4.5

[a] Recorded in d_6 at 30 °C. [b] One of the CH_2 and $SiMe_3$ resonances in the ^1H and ^{13}C NMR spectra, respectively, could not be resolved. [c] See also ref 7b.

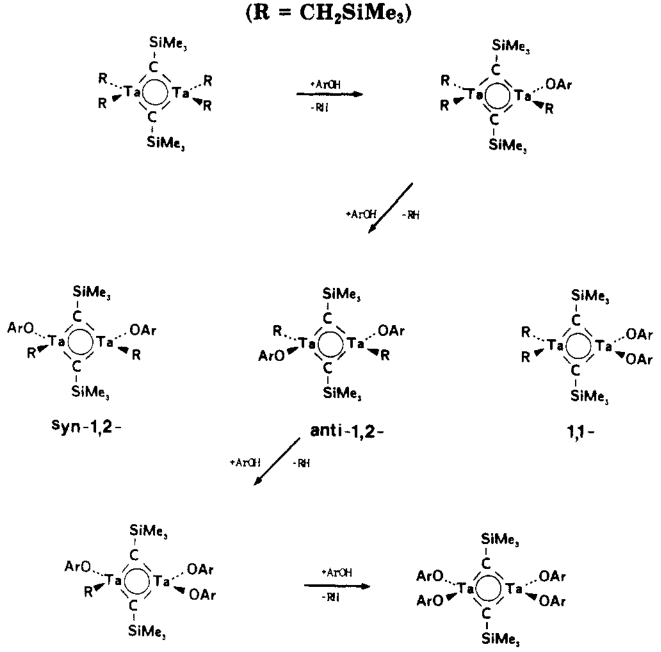
butadiene core intact.[9] We wish to report here our results concerning the reaction of the tantalum dimer with the three reagents 2,6-dimethyl- ($HOAr\text{-}2,6\text{-}Me_2$), 2,6-diphenyl- ($HOAr\text{-}2,6\text{-}Ph_2$), and 2,6-di-*tert*-butylphenol ($HOAr\text{-}2,6\text{-}t\text{-}Bu_2$). The structures of two of the asymmetrically substituted products as well as the somewhat initially surprising inactivity of the bridging alkylidyne function in these compounds for intramolecular activation of the CH bonds of $OAr\text{-}2,6\text{-}t\text{-}Bu_2$ ligands will also be discussed.

Results and Discussion

Synthesis of Compounds. If one assumes that the central, bridging alkylidyne units of the ditantalum compound do not undergo protonation when phenolic reagents are added, it is possible to envisage a total of five substitution products as shown in Scheme I. For the disubstituted compound if one further assumes a pseudotetrahedral environment about the metal then there are three possible isomers, which we will refer to as the 1,1- and syn- and anti-1,2-disubstituted compounds. If the $\mu\text{-}CSiMe_3$ does undergo ready protonation, then a large number of other, possibly mononuclear products could be imagined. With 2,6-dimethylphenol (<5 equiv/Ta) compound 1 was found to react rapidly in hydrocarbon solvents to yield Me_4Si and a mixture of products as judged by ^1H NMR. Addition of 5 or greater equiv of $HOAr\text{-}2,6\text{-}Me_2$/Ta led to the formation of the known compound $Ta(OAr\text{-}2,6\text{-}Me_2)_5$. A ^1H NMR titration of 1 with $HOAr\text{-}2,6\text{-}Me_2$ in benzene-d_6 showed the reaction to proceed through a variety of intermediates, none of which ever became a dominant component. However, the observation of a singlet at δ 9.31 supported the idea that a (trimethylsilyl)methylidene ($Ta{=}CHSiMe_3$) functional group was present in one of the intermediates.

With the more bulky 2,6-diphenylphenol, however, the reaction with 1 was much more controlled. The slow, room-temperature addition of 1 equiv of $HOAr\text{-}2,6\text{-}Ph_2$ to 1 in benzene solution led to the rapid (<10-min) formation of the monosubstituted product $(Me_2SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2(Ta(CH_2SiMe_3)(OAr\text{-}2,6\text{-}Ph_2)$ (2). The deep red compound could be easily recrystallized from warm hexane as large blocks. The aliphatic region of the ^1H NMR spectrum of 2 clearly shows the three nonequivalent $Ta{-}CH_2SiMe_3$ groups as expected for the structure shown (Scheme I). The methylene protons of one of these groups was shifted considerably upfield from its normal position to δ 0.03 (Table I). We assign this resonance as being due to the alkyl group coordinated to the same tantalum atom as the 2,6-diphenylphenoxide. The large diamagnetic anisotropy of the two phenyl substituents in $OAr\text{-}2,6\text{-}Ph_2$ typically causes the upfield shift of the nuclei close by in the coordination sphere.[10] Three types of terminal alkyl groups are also indicated by the ^{13}C NMR spectrum of 2, and again one of the α-carbon atoms is shifted significantly upfield. The characteristic signals due to the two, still equivalent bridging alkylidyne ligands are also present (Table I). Further reaction of 2 with another equivalent of $HOArPh_2$ occurs readily in benzene solution to generate what appears to be a disubstituted product (3) by microanalysis.

Scheme I. Possible Substitution Products from the Reaction of Phenols (ArOH) with $Ta_2(\mu\text{-}CSiMe_3)_2(R)_4$ ($R = CH_2SiMe_3$)



Spectroscopic studies (^1H and ^{13}C NMR) of this red solid 3 are consistent with the presence of all three of the possible substitutional isomers. Hence, 470-MHz ^1H NMR spectra of 3 show six distinct $SiMe_3$ groups of approximately equal intensity. Some of these resonances appear upfield of Me_4Si. Each of the three possible substitution isomers for 3 is expected to contain two types of $SiMe_3$ methyl groups, due to the terminal alkyls and bridging

---

(9) Chisholm, M. H.; Huffman, J. C.; Heppert, J. A. *J. Am. Chem. Soc.* 1985, *107*, 5116.

(10) Coffindaffer, T. W.; Westler, W. M.; Rothwell, I. P. *Inorg. Chem.* 1985, *24*, 4569.

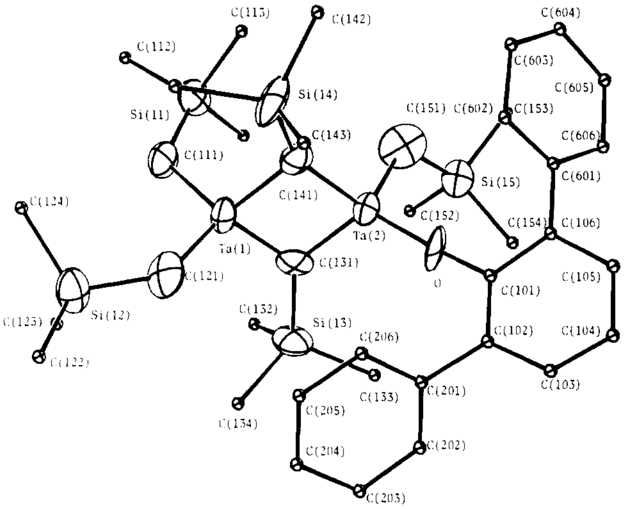


Figure 1. ORTEP drawing of $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)(OAr\text{-}2,6\text{-}Ph_2)]$ (2) emphasizing the central coordination sphere.

alkylidyne. Furthermore the ^{13}C NMR spectrum of 3 shows three distinct alkylidyne carbon resonances at δ 391.4, 387.7, and 385.2 along with three different alkyl resonances at δ 63.5, 64.2, and 74.4. The signal at δ 74.4 we interpret as being due to the alkyl carbons of the 1,1-disubstituted isomer, these alkyls being bound to a tantalum center that does not contain a 2,6-diphenylphenoxide ligand. The other two resonances are hence the alkyl ligands of the syn and anti forms of the 1,2-substitution products, each terminal alkyl now being bound to the same metal as a OAr-2,6-Ph_2 group with its associated diamagnetic anisotropy. Attempts to enrich one of the three components of this mixture were not undertaken.

Chisholm and workers have shown that the tungsten analogue $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$ reacts with *t*-BuOH to give a mixture of two isomers of the disubstituted complex.[9] The disubstituted derivative of 2,6-diphenylphenoxide (3) will only undergo further substitution on heating. Hence heating a toluene solution of 1 with 4 equiv of HOAr-2,6-Ph_2 at 100 °C for 48 h led to a dark green solution of the tetrasubstituted complex $[(2,6\text{-}Ph_2ArO)_2Ta(\mu\text{-}CSiMe_3)_2]_2$ (4). The sparingly soluble compound crystallizes from the reaction mixture on cooling. The intense green color of 4 contrasts with the orange to deep red color found for other derivatives in this study. However, the alkoxide $[(i\text{-}PrO)_2W(\mu\text{-}CSiMe_3)]_2$ synthesized and structurally characterized by Chisholm and co-workers was also an intense green.[9]

The lack of solubility of 4 in hydrocarbon solvents precluded ^{13}C NMR studies. However, 470-MHz ^1H NMR spectra of a very pale green, saturated solution of 4 is benzene-d_6 revealed the μ-CSi*Me*$_3$ protons resonating at δ -0.78. Again the diamagnetic anisotropy of the OAr-2,6-Ph_2 ligand appears to account for this upfield shift of this signal.

With the even more sterically demanding 2,6-di-*tert*-butylphenol (HOAr-2,6-*t*-Bu_2), 1 underwent substitution only on extended heating at 100 °C. Hence a toluene or benzene mixture of 1 and 2 equiv of HOAr-2,6-*t*-Bu_2 when heated at 100 °C for 36 h yielded a deep red solution of a disubstituted complex (5). Although small amounts of a monosubstituted complex could be seen in the ^1H NMR of the reaction mixture at intermediate stages, no attempt was made to isolate it. The ^1H NMR of 5 showed only one set of Ta-CH_2SiMe_3 and Ta-μ-$CSiMe_3$ resonances, indicating the presence of only one of the three possible substitution isomers. Similarly the ^{13}C NMR of 5 indicated only one isomer was present, with the bridging alkylidyne and alkyl carbons resonating at δ 386.3 and 77.3, respectively. Because of the high symmetry of all three of the isomeric forms of the disubstituted compound, it is impossible to differentiate them conclusively by using only ^1H and ^{13}C NMR spectroscopy. However, because of the known bulk of the 2,6-di-*tert*-butylphenoxide group, we initially felt that this ligand would favor the adoption of the anti-1,2-isomer. This assumption was shown to be totally incorrect by an X-ray diffraction study of 5 which showed the molecule to be the asymmetric, 1,1-disubstituted product. The thermal reactivity of 5 and its further reaction with the HOAr-2,6-Bu_2 will be discussed in a later section of this paper.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)(OAr\text{-}2,6\text{-}Ph_2)]$ (2)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ta(1)	0.30422 (4)	0.20997 (4)	0.41275 (1)	3.52 (1)
Ta(2)	0.20470 (4)	0.30261 (3)	0.35015 (1)	3.145 (9)
Si(11)	0.4897 (3)	-0.0070 (3)	0.3691 (1)	4.55 (8)
Si(12)	0.3292 (4)	0.2210 (3)	0.5064 (1)	5.11 (9)
Si(13)	0.4705 (3)	0.4441 (3)	0.3828 (1)	4.71 (8)
Si(14)	0.0189 (3)	0.0957 (3)	0.4030 (1)	5.36 (9)
Si(15)	0.3610 (3)	0.3146 (3)	0.2626 (1)	4.46 (8)
O	0.0781 (7)	0.4111 (6)	0.3452 (2)	4.3 (2)
C(111)	0.442 (1)	0.0781 (9)	0.4092 (4)	4.6 (3)
C(112)	0.589 (2)	-0.127 (1)	0.3806 (5)	7.9 (4)
C(113)	0.344 (1)	-0.060 (1)	0.3488 (4)	6.7 (4)
C(114)	0.590 (1)	0.077 (1)	0.3357 (4)	6.3 (4)
C(121)	0.248 (1)	0.262 (1)	0.4666 (4)	5.1 (3)
C(122)	0.255 (2)	0.296 (1)	0.5455 (5)	8.4 (5)
C(123)	0.507 (2)	0.249 (2)	0.4999 (6)	9.2 (5)
C(124)	0.308 (2)	0.072 (1)	0.5156 (5)	8.3 (5)
C(131)	0.349 (1)	0.3283 (8)	0.3793 (3)	3.4 (2)
C(132)	0.636 (1)	0.389 (1)	0.3727 (5)	7.8 (4)
C(133)	0.444 (1)	0.555 (1)	0.3512 (5)	7.9 (4)
C(134)	0.457 (2)	0.504 (1)	0.4283 (5)	9.4 (5)
C(141)	0.155 (1)	0.1852 (8)	0.3844 (3)	3.5 (2)
C(142)	-0.032 (1)	0.003 (1)	0.3680 (5)	9.0 (5)
C(143)	-0.123 (1)	0.182 (1)	0.4202 (6)	9.8 (5)
C(144)	0.068 (1)	0.010 (1)	0.4401 (4)	7.6 (4)
C(151)	0.279 (1)	0.231 (1)	0.3000 (3)	3.9 (3)
C(152)	0.537 (1)	0.325 (1)	0.2679 (5)	6.8 (4)
C(153)	0.342 (1)	0.246 (1)	0.2192 (4)	6.9 (4)
C(154)	0.293 (1)	0.453 (1)	0.2609 (5)	6.6 (4)
C(101)	-0.0120 (9)	0.4870 (9)	0.3387 (4)	4.1 (3)
C(102)	-0.029 (1)	0.5783 (9)	0.3600 (3)	4.3 (3)
C(103)	-0.113 (1)	0.659 (1)	0.3500 (4)	5.5 (3)
C(104)	-0.175 (1)	0.652 (1)	0.3202 (4)	5.9 (3)
C(105)	-0.162 (1)	0.557 (1)	0.3000 (4)	6.0 (3)
C(106)	-0.0810 (9)	0.471 (1)	0.3087 (3)	4.2 (3)
C(201)	0.034 (1)	0.5906 (9)	0.3933 (4)	4.5 (3)
C(202)	0.100 (1)	0.683 (1)	0.4012 (4)	6.6 (4)
C(203)	0.149 (2)	0.701 (1)	0.4335 (5)	8.8 (5)
C(204)	0.133 (2)	0.618 (2)	0.4590 (5)	10.5 (5)
C(205)	0.070 (2)	0.526 (1)	0.4523 (4)	7.6 (4)
C(206)	0.024 (1)	0.510 (1)	0.4199 (4)	5.8 (3)
C(601)	-0.072 (1)	0.371 (1)	0.2866 (3)	4.4 (3)
C(602)	-0.091 (1)	0.270 (1)	0.3025 (4)	4.8 (3)
C(603)	-0.091 (1)	0.175 (1)	0.2820 (4)	5.6 (3)
C(604)	-0.065 (1)	0.182 (1)	0.2454 (4)	6.2 (3)
C(605)	-0.047 (1)	0.283 (1)	0.2304 (4)	6.3 (4)
C(606)	-0.051 (1)	0.376 (1)	0.2502 (4)	5.9 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)\,B(1,2) + ac(\cos\beta)\,B(1,3) + bc(\cos\alpha)\,B(2,3)]$.

Solid-State Structures of 2 and 5. An ORTEP view of each of these molecules is given in Figures 1 and 2, respectively, along with the numbering scheme used. The fractional coordinates and isotropic thermal parameters are given in Tables II and III while selected bond distances and angles are given in Tables IV and V. Table VI con-

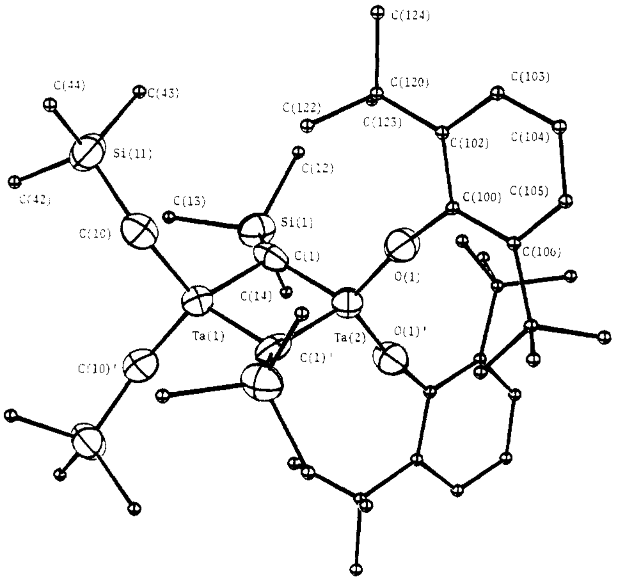


Figure 2. ORTEP drawing of $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2]$ (**5**) emphasizing the central coordination sphere.

Table III. Fractional Coordinates and Isotropic Thermal Parameters for $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2]$ (5)[a]

atom	x	y	z	B, Å^2
Ta(1)	0	0.29179 (1)	1/4	1.119 (5)
Ta(2)	0	0.16909 (1)	1/4	0.934 (5)
Si(1)	0.2556 (1)	0.23944 (7)	0.25680 (9)	1.24 (3)
Si(11)	−0.0371 (1)	0.38150 (8)	0.0821 (1)	1.46 (3)
O(1)	0.0489 (3)	0.1301 (2)	0.1597 (2)	1.33 (7)
C(1)	0.1068 (5)	0.2306 (2)	0.2737 (3)	1.2 (1)
C(2)	0.3348 (5)	0.2033 (3)	0.3351 (4)	2.1 (1)
C(3)	0.2992 (5)	0.3154 (3)	0.2568 (4)	1.9 (1)
C(4)	0.2946 (5)	0.2086 (3)	0.1600 (4)	1.8 (1)
C(10)	0.0502 (6)	0.3397 (3)	0.1496 (4)	1.8 (1)
C(12)	−0.0945 (6)	0.4410 (3)	0.1394 (4)	2.3 (1)
C(13)	−0.1503 (6)	0.3391 (3)	0.0407 (4)	2.3 (1)
C(14)	0.0435 (6)	0.4109 (4)	−0.0009 (4)	2.6 (1)
C(101)	0.0844 (5)	0.0943 (3)	0.1032 (3)	1.3 (1)
C(102)	0.0511 (5)	0.1046 (3)	0.0249 (3)	1.3 (1)
C(103)	0.0838 (5)	0.0661 (3)	−0.0312 (4)	1.8 (1)
C(104)	0.1463 (6)	0.0195 (3)	−0.0123 (4)	2.0 (1)
C(105)	0.1798 (5)	0.0118 (3)	0.0623 (4)	1.9 (1)
C(106)	0.1513 (5)	0.0480 (3)	0.1232 (4)	1.5 (1)
C(120)	−0.0147 (4)	0.1568 (3)	0.0016 (3)	1.5 (1)
C(121)	−0.0323 (6)	0.1593 (3)	−0.0866 (4)	2.3 (1)
C(122)	0.0458 (6)	0.2104 (3)	0.0245 (4)	1.9 (1)
C(123)	−0.1281 (5)	0.1549 (3)	0.0381 (4)	1.7 (1)
C(160)	0.2007 (5)	0.0327 (3)	0.2011 (4)	1.6 (1)
C(161)	0.1665 (6)	0.0687 (3)	0.2718 (4)	1.9 (1)
C(162)	0.3246 (5)	0.0374 (3)	0.1947 (4)	2.3 (1)
C(163)	0.1691 (6)	−0.0291 (3)	0.2236 (4)	2.4 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

tains a comparison of some important bond distances and angles in **2** and **5** with those of other related molecules in the literature. Although compound **1** has not been the subject of a full structure determination, the niobium analogue was and **1** has been shown to be isomorphous with it.[7] The difference between the covalent radii of Nb and Ta is small, and hence comparison of **2** and **5** with this structure is reasonably valid. The Ta–Ta distances of 2.8825 (6) and 2.9071 (4) Å for **2** and **5** compare well with the value of 2.897 (2) Å found for the niobium alkyl dimer (Table VI). The distance has to be considered a nonbonding value as is to be expected for these d^0–d^0 dimers, especially in view of the much shorter values found for the metal–metal distances in tungsten (d^1–d$^{1\prime}$)[8] and rhenium (d^2–d^2) analogues.[11] The terminal Ta–CH_2SiMe_3 distances all fall in the range 2.14–2.16 Å, similar to other tantalum(V)–alkyl distances such as 2.17 (2) Å in $Ta(OAr\text{-}2,6\text{-}Bu_2)_2(=CHSiMe_3)(CH_2SiMe_3)$ and 2.155 (10) Å in $Ta(OAr\text{-}2,6\text{-}Me_2)_4(CH_3)$.[12] The Ta–O distances of 1.885 (6) and 1.904 (4) for **2** and **5**, respectively are much smaller than the Ta–C distances to the terminal alkyls. This shortening as well as the large Ta–O–Ar angles have been attributed to the significance of oxygen-p to metal-d π-

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)(OAr\text{-}2,6\text{-}Ph)]$ (2)

	Bond Distances		
Ta(1)–Ta(2)	2.8825 (6)		
Ta(1)–C(111)	2.15 (1)	Ta(2)–O	1.885 (6)
Ta(1)–C(121)	2.14 (1)	Ta(2)–C(131)	1.96 (1)
Ta(1)–C(131)	1.93 (2)	Ta(2)–C(141)	1.96 (1)
Ta(1)–C(141)	1.980 (9)	Ta(2)–C(151)	2.15 (1)
	Bond Angles		
Ta(1)–Ta(2)–O	131.6 (2)	Ta(2)–Ta(1)–C(111)	122.3 (3)
Ta(1)–C(131)–O	42.0 (3)	Ta(2)–Ta(1)–C(121)	124.5 (3)
Ta(1)–C(141)–O	43.2 (3)	Ta(2)–Ta(1)–C(131)	42.5 (3)
Ta(1)–C(151)–O	115.2 (3)	Ta(2)–Ta(1)–C(141)	42.6 (3)
Ta(1)–C(131)–Ta(2)	95.6 (5)	Ta(1)–C(141)–Ta(2)	94.1 (4)
C(111)–Ta(1)–C(121)	113.2 (4)	C(121)–Ta(1)–C(131)	114.4 (5)
C(111)–Ta(1)–C(131)	114.0 (5)	C(121)–Ta(1)–C(141)	113.5 (4)
C(111)–Ta(1)–C(141)	113.7 (4)	C(131)–Ta(1)–C(141)	85.1 (4)
O–Ta(2)–C(131)	121.2 (3)	C(131)–Ta(2)–C(141)	85.1 (5)
O–Ta(2)–C(141)	116.1 (3)	C(131)–Ta(2)–C(151)	109.2 (4)
O–Ta(2)–C(151)	113.1 (4)	C(141)–Ta(2)–C(151)	108.8 (4)
Ta(1)–C(111)–Si(11)	126.2 (6)	Ta(1)–C(131)–Si(13)	128.7 (6)
Ta(1)–C(121)–Si(12)	125.4 (6)	Ta(2)–C(131)–Si(13)	134.5 (6)
Ta(2)–C(151)–Si(15)	122.0 (5)	Ta(1)–C(141)–Si(14)	119.4 (6)
Ta(2)–O–C(101)	175.1 (8)	Ta(2)–C(141)–Si(14)	144.4 (5)

Table V. Selected Bond Distances (Å) and Angles (deg) for $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2]$ (5)

	Bond Distances		
Ta(1)–Ta(2)	2.9071 (4)	Ta(1)–C(1)	1.997 (6)
Ta(1)–C(10)	2.157 (6)	Ta(2)–C(1)	2.002 (6)
Ta(2)–O(1)	1.904 (4)		
	Bond Angles		
Ta(1)–Ta(2)–O(1)	119.0 (1)	Ta(2)–Ta(1)–C(1)	43.4 (2)
Ta(1)–Ta(2)–C(1)	43.3 (2)	Ta(2)–Ta(1)–C(10)	121.8 (2)
Ta(1)–C(1)–Ta(2)	93.2 (2)	C(1)–Ta(1)–C(1)′	86.9 (3)
C(1)–Ta(1)–C(10)	111.0 (3)	C(1)′–Ta(1)–C(10)	116.5 (4)
C(10)–Ta(1)–C(10)′	116.5 (4)	O(1)–Ta(2)–O(1)′	122.0 (2)
O(1)–Ta(2)–C(1)	108.2 (2)	O(1)–Ta(2)–C(1)′	113.2 (2)
C(1)–Ta(2)–C(1)′	86.6 (3)	Ta(1)–C(1)–Si(1)	122.1 (3)
Ta(1)–C(10)–Si(11)	127.9 (4)	Ta(2)–C(1)–Si(1)	133.9 (4)
Ta(2)–O(1)–C(101)	170.1 (4)		

Table VI. Metal–Metal Bond Distances for Known 1,3-Dimetallacyclobutadiene Derivatives

compd	M–M, Å	ref
$[(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)]_2$	2.897 (2)	7
2	2.8825 (6)	this work
5	2.9071 (4)	this work
$[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$	2.535 (10)	8
$[(i\text{-}PrO)_2W(\mu\text{-}CSiMe_3)]_2$	2.618 (2)	9
	2.622 (2)	
$[(t\text{-}BuO)_2W(\mu\text{-}CPh)]_2$	2.665 (1)	16
$[(Me_3SiCH_2)_2Re(\mu\text{-}CSiMe_3)]_2$	2.557 (1)	11

---

[11] Bochmann, M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul-Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1797.

[12] (a) Chamberlain, L. R.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.*, in press. (b) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 7338.

bonding and is a characteristic of high-valent, early-transition-metal alkoxide and aryloxide chemistry.[13–15]

The distance to the bridging alkylidyne carbon atoms are of interest. For tungsten, three different μ-alkylidyne compounds of formula $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$,[8] $[(t\text{-}BuO)_2W(\mu\text{-}CPh)]_2$,[16] and $[(i\text{-}PrO)_2W(\mu\text{-}CSiMe_3)]_2$[9] have been structurally characterized. For the alkoxide derivatives the W–W distances of 2.665 (1) and 2.620 (2) Å, respectively are significantly longer than for the alkyl complex, 2.535 (10) Å. This lengthening of the formal metal–metal single bond for the alkoxide d^1–d^1 dimers was argued to be a consequence of the presence of oxygen-p to metal-d π-bonding causing a weakening of the metal–metal interaction. In the case of the phenoxide derivatives **2** and **5** which contain no formal metal–metal interaction it can be seen that the tantalum–tantalum distance does not undergo any dramatic elongation. Furthermore, the distance to the $\mu\text{-}CSiMe_3$ carbon atoms in **5** are essentially identical for both the $(R)_2Ta$ and $(ArO)_2Ta$ fragments. Hence it would appear that the substitution of aryloxide for alkyl ligands has little effect on bond distance between the tantalum atom and the $\mu\text{-}CSiMe_3$ groups. This result, therefore, seems to confirm the idea that the elongation of the metal–metal distance in the tungsten dimers is a consequence of the effect the oxygen donor ligands have on the metal–metal single bond.

The delocalized nature of the 1,3-dimetallacyclobutadiene central core of the molecules results in an assignment of 1.5 for the $Ta\text{-}\mu\text{-}CSiMe_3$ bond order. The coordination environment of Ta(2) in $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2]$ (**5**) can be compared with that found in $(ArO\text{-}2,6\text{-}t\text{-}Bu_2)_2Ta({=}CH_2SiMe_3)(CH_2SiMe_3)$.[12] The latter mixed alkyl–alkylidene contains both a discrete single and double bond, while **5** contains two bonds of formal order 1.5 both bound to a $Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2$ unit. The $Ta\text{-}\mu\text{-}CSiMe_3$ distance of 1.997 (6) Å in **5** does fall as expected between the values of 1.89 (3) and 2.17 (2) Å found for the double and single bonds in $(t\text{-}Bu_2\text{-}2,6\text{-}ArO)_2Ta({=}CHSiMe_3)(CH_2SiMe_3)$.

Although the asymmetric substitution in **2** and **5** does not lead to any significant dissimilarity in the $Ta\text{-}\mu\text{-}CSiMe_3$ distances, there is another noticeable asymmetry to the bridging ligands. This can be seen by comparing the Ta-μ-C–Si angles for the two ends of the molecule. For monosubstituted **2** values of 134.5 (6) and 144.4 (5)° are found for this angle to the substituted tantalum compared to values of 128.7 (6) and 119.4 (6) found for this angle to the unsubstituted metal atom. Similarly in **5** the corresponding angles are 133.9 (3) and 122.1 (3)°. Therefore, there is a definite bending of the $SiMe_3$ substituents of the bridging alkylidyne ligands away from these bulky phenoxide substituents. Given the similarity of the $Ta\text{-}\mu\text{-}CSiMe_3$ distances we see little electronic rationale for this effect. This observation, however, leads to a consideration of the substitution patterns that we have found in this study.

Substitution Patterns for $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)]_2$ (1). The rate of substitution of the terminal alkyl groups in **1** is, not surprisingly, strongly dependent on the steric demands of the phenolic reagent. After the initial introduction of one aryloxide substituent there are now three differing sites at which subsequent protonolysis by a second phenol can take place. In the case of 2,6-diphenylphenol, all three positions in the monosubstituted derivative **2** appear to be equally susceptible to substitution. Hence, an approximately equal mixture of the 1,1-, syn-1,2-, and anti-1,2-disubstituted derivatives is found when **2** reacts with an extra equivalent of $HOAr\text{-}2,6\text{-}Ph_2$ to give **3**. However, with the more bulky 2,6-di-*tert*-butylphenol, the disubstituted complex was found by X-ray diffraction to be the asymmetric 1,1 compound **5**. On steric reasoning this appears to be the opposite isomer that one would predict, containing both bulky aryloxides on the same metal center. Spectroscopic analysis (^1H and ^{13}C NMR) failed to detect any of the other substitution isomers even in the crude product mixture. The result obtained with 2,6-diphenylphenoxide argues strongly against an electronic effect being the cause of the formation of this isomer for **5**. If the initial coordination of a phenoxide ligand was to electronically enhance substitution, then one would have also seen the 1,1-disubstitution isomer predominating for **3**. We believe a more reasonable, although not totally compelling, rationalization of this result lies in a steric argument in which the substitution of a bulky phenoxide ligand at one end of the ditantalum unit sterically suppresses substitution at the other end! The bulky phenoxide would do this by bending the $SiMe_3$ substituents of the bridging alkylidyne units toward the other tantalum atom as is observed in the solid state for **2** and **5**. Support for the idea that 2,6-di-*tert*-butylphenoxide ligands severely hinder substitution at the other end of the dimer to which they are attached comes from the observed reactivity of **5**. Although the unsubstituted tantalum metal center in **5** appears to be very similar to those in the parent alkyl **1**, it requires much more extreme conditions to undergo further reaction with $HOAr\text{-}2,6\text{-}t\text{-}Bu_2$ (vide infra).

Coordination Properties of 2,6-Di-*tert*-butylphenoxide. The crystallographically imposed C_2 axis passing through the two tantalum atoms of **5** result in both 2,6-di-*tert*-butylphenoxide ligands being equivalent. However, the aryloxide ligand in this molecule is anything but symmetric. This asymmetry centers on the observed differing conformations of the two *tert*-butyl substituents. For one of the groups, centered on C(120), a "normal" conformation is found such that the distance between the metal atom and its methyl groups are maximized. This is as one would expect for this bulky substituent, sterically interacting unfavorably with both the metal and its substituents. However, the other *tert*-butyl group has adopted the exact opposite conformer, with a unique methyl group pointing directly toward the metal center. This situation would be expected to maximize any unfavorable steric interactions. An initial room-temperature X-ray diffraction study on **5** indicated this intriguing conformation but was not suitable for any accurate hydrogen atom refinement to be attempted. Hence, a low-temperature data set was collected, and both the non-hydrogen and hydrogen atoms were refined. An ORTEP view of the 2,6-di-*tert*-butylphenoxide ligand in **5** is shown in Figure 3 emphasizing the metal coordination sphere. The hydrogen atoms refined for the unique methyl group C(161) have also been included. Of the 20 or so X-ray diffraction studies we have carried out on high-valent group 4 or 5 metal compounds containing approximately 30 nonequivalent 2,6-di-*tert*-butylphenoxides, we have observed the unusual conformation found in **5** in only two other complexes. These are $Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2Cl_3$[2] and $Zr(OAr\text{-}2,6\text{-}t\text{-}Bu_2)(OAr\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}OMe)(CH_2Ph)_2$ ($OAr\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}OMe$ = 4-methoxy-2,6-di-*tert*-butylphenoxide).[17] The unusual aryloxides

---

(13) Chisholm, M. H. *Polyhedron* **1983**, 2, 681.

(14) Coffindaffer, T. W.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. *J. Chem. Soc., Chem. Commun.* **1985**, 1519.

(15) For a review of metal alkoxide chemistry see: Bradley, D. C.; Mehrotra, R. C.; Gavr, D. P. *Metal Alkoxides*; Academic: London, New York, San Francisco, 1978.

(16) Cotton, F. A.; Schwotzer, W.; Shramshaum, E. S. *Organometallics* **1983**, 2, 1167.

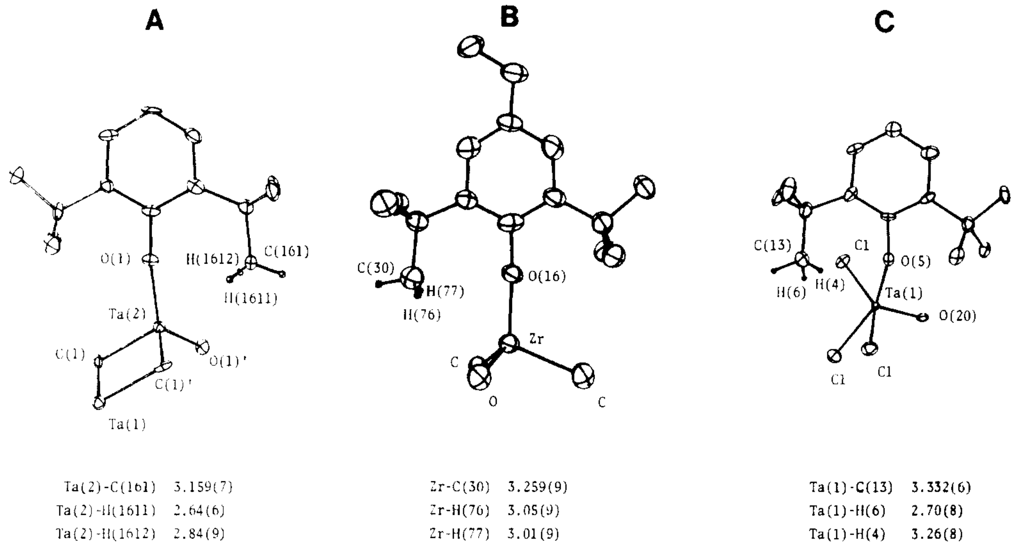


Figure 3. ORTEP drawings showing the conformation of one of the *tert*-butyl groups of an 2,6-di-*tert*-butylphenoxide ligand in the following complexes: A, $[(Me_3CH_2Si)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2]$ (5); B, $Zr(OAr\text{-}2,6\text{-}t\text{-}Bu_2)(OAr\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}OMe)(CH_2Ph)_2$; C, $Ta(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2Cl_3$.

in these complexes are also shown in Figure 3. The distance to the close carbon atoms in these three compounds varies from 3.159 (7) to 3.332 (6) Å. There is now a growing body of literature that indicates that high-valent, electron-deficient, early d-block, lanthanide or actinide metal complexes can exhibit ground-state bonding interactions with hydrocarbon fragments of coordinated ligands.[18-20] The situation, for which the term *agostic* has been proposed,[18] involves the donation of electron density from carbon–hydrogen bonds to suitable empty orbitals on the metal center.[21-23] In all three phenoxide structures the hydrogen atoms were refined, and those on the unique methyl group are shown in Figure 3. It can be seen that none of the carbon–hydrogen bonds are bent directly toward the metal in a linear M–H–C fashion. Instead there are typically two hydrogens closer to the metal than the third. Distances vary between 2.64 (6) and 3.26 (8) Å. The closest approach is for one of the hydrogens in 5. This distance can be compared to tantalum–hydride bonds of ≃1.7 Å. Although the contacts in 5 are close, the following points seem to argue against an agostic interaction. First, the crystallographic symmetry of 5 means that there are in fact two equivalent *tert*-butyl methyl groups close to the same metal center. It seems unlikely that two positive metal–hydrocarbon interactions would take place. Secondly, analysis of the bond angles about the central carbon of the *tert*-butyl group shows that the Ar–C–CH_3 angle to the unique methyl group is significantly larger than normal in all three cases. This implies that the metals are in fact pushing these methyl groups away from themselves. We, therefore, conclude that it is possible for 2,6-di-*tert*-butylphenoxide ligands to coordinate in such a way that very close metal–methyl contacts can occur in the ground state but that there is little or no evidence that these contacts are anything but repulsive. However, these observed conformational situations are clearly relevant to the observed cyclometallation chemistry of this ligand in which these particular CH bonds are, sometimes under very mild conditions, activated and cleaved.[4]

Thermal Cyclometalation of 2,6-Di-*tert*-butylphenoxide in $[(t\text{-}Bu_2\text{-}2,6\text{-}ArO)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2]$ (5). Despite the observation of a close Ta···CH_3 contact in the solid state and the expectation of alkylidyne units being potent functional groups for CH bond activation, compound 5 is surprisingly thermally robust. Heating sealed 5-mm NMR tubes of 5 in toluene-d_8 at temperatures of 150 °C or above, however, did lead to its disappearance from solution as judged by ^1H NMR. The products of this thermolysis were mainly Me_4Si and the phenol $HOAr\text{-}2,6\text{-}t\text{-}Bu_2$ along with a large number of small components. One of these components was identified as the known bis-cyclometalated complex $Ta(OC_6H_3\text{-}t\text{-}Bu_2CMe_2CH_2)_2(CH_2SiMe_3)$[12] by 470-MHz ^1H NMR. The amount of this product was estimated as only 5% of the initial amount of 5 in solution. The thermolysis of 5 with two more equivalents of $HOAr\text{-}2,6\text{-}t\text{-}Bu_2$ under similar conditions did appear to increase the amount of this product, but large amounts of Me_4Si and other unidentified products were also still produced. This behavior contrasts with that of $(t\text{-}Bu_2\text{-}2,6\text{-}ArO)_2Ta({=}CHSiMe_3)(CH_2SiMe_3)$ which undergoes thermal cyclometalation rapidly at 80 °C to produce the complex $Ta(OC_6H_3\text{-}t\text{-}Bu_2CMe_2CH_2)_2(CH_2SiMe_3)$ in very good yield, liberating 1 equiv of Me_4Si.[12] The lack of ready cyclometalation of the $OAr\text{-}2,6\text{-}t\text{-}Bu_2$ ligands in 5 was initially surprising. However, analysis of possible reaction pathways for the complex based on accepted mechanistic ideas[24-26] indicates

---

(17) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902.

(18) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395 and references therein.

(19) Dawood, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 802.

(20) Erker, G.; Fromberg, W.; Angermund, K.; Schlund, R.; Kruger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372.

(21) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 2154.

(22) (a) Colvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (b) Williams, J. M.; Brown, R. K.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D. *J. Am. Chem. Soc.* **1978**, *100*, 7407. (c) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4542.

(23) (a) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117. (b) Trofimekno, S. *J. Am. Chem. Soc.* **1968**, *90*, 4754; *Inorg. Chem.* **1970**, *9*, 2483. (c) Cotton, F. A.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 5074.

(24) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1.

(25) (a) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425. (b) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (c) Marks, T. J.; Day, V. W. In *Fundamental and Technological Aspects of Organo-Element Chemistry*; D. Reidel Publishing: Boston, 1985 and references therein.

(26) (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (b) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

Table VII. Crystal Data and Data Collection Parameters

	2	5
formula	$Ta_2Si_5OC_{38}H_{64}$	$Ta_2Si_4O_2C_{44}H_{82}$
fw	1039.26	1117.38
space group	$P2_1/n$	P_{bcn}
a, Å	10.343 (1)	12.283 (6)
b, Å	12.209 (2)	23.692 (6)
c, Å	37.411 (6)	17.205 (6)
β, deg	84.23 (1)	
V, Å^3	4700 (2)	5007 (5)
Z	4	4
d_{calcd}, g cm^{-3}	1.469	1.482
cryst dimens, mm	0.61 × 0.26 × 0.23	0.65 × 0.40 × 0.36
temp, °C	23.0	−160.0
radiatn (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromater	graphite	graphite
linear abs coef, cm^{-1}	47.49	44.42
abs correctn applied	empirical[a]	empirical[a]
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	θ–2θ	θ–2θ
h,k,l limits	−12 to 12, 0 to 14, 0 to 44	0 to 17, 0 to 33, 0 to 24
2θ range, deg	3.00–50.00	4.00–60.00
scan width, deg	0.70 + 0.35 tan θ	0.90 + 0.35 tan θ
takeoff angle, deg	5.00	4.90
programs used	Enraf-Nonius SDP	Enraf-Nonius SDP
F_{000}	2064.0	2256.0
ρ factor used in weighting	0.060	0.070
unique data	8690	7306
data with $I > 3.0\sigma(I)$	4597	4118
no. of variables	415	408
largest shift/esd in final cycle	0.15	0.32
R	0.042	0.038
R_w	0.056	0.056
goodness of fit	1.440	1.204

[a] Flack, H. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1977**, *A33*, 890.

problems with the reaction. First, it may be that it is difficult for the transition state to form due to the strict constraints placed on the μ-$CSiMe_3$ groups to which the hydrogen of the activated CH bond is to be transferred. Secondly, it is difficult to envisage a very happy leaving group for **5**. The product of cyclometalation of one aryloxide in **5** would be an alkylidene complex [$Ta(OC_6H_3$-t-$BuCMe_2CH_2)$(OAr-2,6-t-Bu_2)(=$CHSiMe_3$)] as well as a fragment [$(Me_3SiCH_2)_2Ta(\equiv CSiMe_3)$]. The fragments may be associated together. However, eventually the latter, unsaturated fragment will have to be lost. This presumably will make the reaction enthalpically more difficult. These two restrictions coupled together are the probable cause for the lack of facile cyclometalation of the aryloxide ligands in **5**.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere either in a Vacuum Atmospheres dri-lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone under a nitrogen atmosphere [$(Me_3SiCH_2)_2Ta(\mu$-$CSiMe_3)]_2$ (**1**) was synthesized by literature methods. Phenolic reagents were purchased (Aldrich) and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Varian Associates XL-200 and Nicolet Instruments 470-MHz spectrometers. Analyses were performed by the Purdue Microanalytical Service and Galbraith Labs.

Preparation of [$(Me_3SiCH_2)_2Ta(\mu$-$CSiMe_3)_2Ta$-(CH_2SiMe_3)(OAr-2,6-Ph_2)] (2). To a solution of **1** (420 mg, 0.5 mmol) in toluene was slowly added a solution of 2,6-diphenylphenol (125 mg, 0.5 mmol) in toluene. The resulting deep red solution was stirred for 1 h before the solvent was removed in vacuo. Extraction of the resulting residue with hexane followed by cooling to −15 °C yielded large red blocks of product; yield 410 mg (79%). Anal. Calcd for $Ta_2Si_5OC_{38}H_{64}$: C, 43.90; H, 6.21. Found: C, 43.91; H, 6.08.

Preparation of the Isomeric Mixture of [$Ta_2(\mu$-$CSiMe_3)_2(CH_2SiMe_3)_2$(OAr-2,6-$Ph_2)_2$] (3). Essentially identical procedures to that used to prepare **2** using 2 equiv of HOAr-2,6-Ph_2 yielded the isomeric mixture **3**. The compound formed an orange-red oil when the hexane extract was evaporated. However, this oil solidified on standing. Yield was essentially quantitative on the basis of the amount of **1** used. Anal. Calcd for $Ta_2Si_4O_2C_{52}H_{66}$: C, 52.15; H, 5.56. Found: C, 52.56; H, 5.90.

Preparation of [(Ph_2-2,6-ArO)$_2Ta(\mu$-$CSiMe_3)]_2$ (4). A mixture of **1** (420 mg, 0.5 mmol) and HOAr-2,6-Ph_2 (500 mg, 2 mmol) was mixed in toluene, and the resulting red solution was heated at 100 °C for 48 h. The resulting deep green solution was allowed to cool yielding dark green daggers of the product; yield 685 mg (91%). Anal. Calcd for $Ta_2Si_2O_4C_{80}H_{70}$: C, 63.47; H, 4.67. Found: C, 63.27; H, 4.74.

Preparation of [$(Me_3SiCH_2)_2Ta(\mu$-$CSiMe_3)_2Ta$(OAr-2,6-t-$Bu_2)_2$] (5). To a solution of **1** (840 mg, 1 mmol) in toluene was added HOAr-2,6-t-Bu_2 (420 mg, 2 mmol), and the mixture was heated at 100 °C for 24 h. The resulting solution was evaporated under vacuum, and the crude red product was taken up in hexane, filtered, and cooled to −15 °C to give well-formed red blocks of the product; yield 670 mg (59%). Anal. Calcd for $Ta_2Si_4O_2C_{44}H_{82}$: C, 47.30; H, 7.40. Found: C, 47.23; H, 7.16.

Thermolysis of 5. Solutions of **5** either with or without added excess HOAr-2,6-t-Bu_2 in toluene-d_8 were sealed into 5-mm ^1H NMR tubes before being heated at 150 °C. The disappearance of **5** was monitored, and the final product (typically after 5–10 h) solution was analyzed by a 470-MHz ^1H NMR spectrometer.

X-ray Structure Determinations. Crystals were aligned and indexed, and data were collected on an Enraf-Nonius CAD-4 diffractometer. For room-temperature data collection, crystals were handled in deoxygenated Nujol and were mounted in appropriate sized glass capillaries surrounded by epoxy resin. For low-temperature data collection, crystals were handled under argon and mounted on the end of a glass fiber by using epoxy resin. The details of data collection and structure refinement are given in Table VII.

Initial atom positions were determined from Patterson maps, and all non-hydrogen atoms were found from subsequent difference Fourier maps. After the positions and anisotropic thermal parameters converged, the positions of the hydrogen atoms were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. In the use of methyl groups, one hydrogen was found from the difference Fourier map and its position was idealized by assuming it was in the plane defined by R–C–H, made a 109.5° bond angle and 0.95-Å bond length. The positions of the two remaining hydrogens were then calculated. Except in the case of compound **5**, the hydrogen positions and temperature factors were fixed during the remainder of the refinement.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8612063) to I.P.R. for support of this research. We also thank the National Scienc Foundation Chemical Instrumentation Program (Grant CHE-8204994) for support of the X-ray diffraction facility at Purdue, I.P.R. also gratefully acknowledges the Camille and Henry Dreyfus Foundation for the award of a Teacher–Scholar Grant and the Alfred P. Sloan Foundation for a fellowship.

Supplementary Material Available: Tables of positional parameters, general temperature factors, bond distances, and bond angles for **2** and **5** (30 pages); listing of structure factor amplitudes for **2** and **5** (38 pages). Ordering information is given on any current masthead page.

Reactions of Decaborane(14) with Silylated Acetylenes. Synthesis of the New Monocarbon Carborane 9-Me_2S-7-[$(Me_3Si)_2CH$]-$CB_{10}H_{11}$

Robin L. Ernest, William Quintana, Robert Rosen, Patrick J. Carroll, and Larry G. Sneddon*

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Received July 7, 1986

The dimethyl sulfide promoted reactions of decaborane(14) with the silylated acetylenes, bis(trimethylsilyl)acetylene and (trimethylsilyl)propyne, have been studied and were not found to yield the expected *ortho*-carborane derivatives but instead gave either alkenyldecaborane or monocarbon carborane products. Thus, the reaction of decaborane(14) with dimethyl sulfide and bis(trimethylsilyl)acetylene produced 9-$(CH_3)_2S$-7-[$((CH_3)_3Si)_2CH$]-$CB_{10}H_{11}$ (I) and 5-$(CH_3)_2S$-6-[$((CH_3)_3Si)_2C{=}CH$]-$B_{10}H_{11}$ (II) while the analogous reaction with (trimethylsilyl)propyne yielded 5-$(CH_3)_2S$-6-[$(CH_3)_3Si(CH_3)C{=}CH$]-$B_{10}H_{11}$ (III). A single-crystal X-ray determination of III demonstrated that compounds II and III result from acetylene hydroboration reactions and have structures based on a decaborane(14) geometry with a dimethyl sulfide bound to the 5-boron and an alkenyl group bound to the 6-boron on the open face. Crystal data for III: space group $P\bar{1}$; $Z = 4$; $a = 16.406$ (4) Å, $b = 16.677$ (5) Å, $c = 8.627$ (2) Å, $\alpha = 100.67$ (2)°, $\beta = 97.78$ (2)°, $\gamma = 118.23$ (2)°, $V = 1974.9$ Å^3; $R = 0.077$ and $R_w = 0.103$ for the 5208 reflections having $F_o^2 > 3\sigma(F_o^2)$. The data obtained for compound I indicate that it is an unusual monocarbon carborane resulting from the insertion of only one of the acetylenic carbons of the bis(trimethylsilyl)acetylene into the cage structure. The cluster geometry is based on an icosahedron missing one vertex, with an exopolyhedral bis(trimethylsilyl)methyl group bonded to the cage carbon. The reaction of I with either NaH, $LiEt_3BH$, Na, or $(\eta^5\text{-}C_5H_5)_2Co$ results in hydrogen loss, dimethyl sulfide dissociation, and cage closure to yield the 2-$((CH_3)_3Si)_2CH$-$CB_{10}H_{10}^-$ anion. A single-crystal X-ray determination of the cobaltocenium salt VI established that the compound has a closo structure based on an octadecahedron, with the cage carbon occupying the four-coordinate 2-position in the structure. Crystal data for VI: space group $P2_1/n$; $Z = 4$; $a = 12.260$ (1) Å, $b = 17.252$ (3) Å, $c = 13.701$ (3) Å, $\beta = 107.94$ (1)°; $V = 2757.0$ Å^3; $R = 0.058$ and $R_w = 0.068$ for the 3061 reflections having $F_o^2 > 3\sigma(F_o^2)$. Thermolysis of I at toluene reflux yielded as the major product 6-$(CH_3)_2S$-2-[$((CH_3)_3Si)_2CH$]-$CB_{10}H_9$ (VII) while thermolysis of I in the solid phase gave VII and small amounts of 6-$(CH_3)_2S$-4-OH-2-[$((CH_3)_3Si)_2CH$]-$CB_{10}H_8$ (VIII). Compounds VII and VIII are isoelectronic with VI, and single-crystal X-ray determinations confirmed that VII and VIII have similar octadecahedral structures. Crystal data for VII: space group $P\bar{1}$; $Z = 2$; $a = 8.834$ (3) Å, $b = 19.211$ (2) Å, $c = 6.998$ (1) Å, $\alpha = 96.20$ (1)°, $\beta = 109.63$ (2)°, $\gamma = 91.91$ (2)°; $V = 1108.9$ Å^3; $R = 0.067$ and $R_w = 0.081$ for the 2864 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for VIII: space group $P\bar{1}$; $Z = 4$; $a = 13.729$ (1) Å, $b = 16.345$ (2) Å, $c = 10.880$ (1) Å, $\alpha = 96.62$ (1)°, $\beta = 93.45$ (1)°, $\gamma = 74.47$ (1)°; $V = 2335.4$ Å^3; $R = 0.065$ and $R_w = 0.078$ for the 5623 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The reaction of decaborane(14) with an alkyne in the presence of dimethyl sulfide is a well-established route to *ortho*-carborane 1,2-$C_2B_{10}H_{12}$ and its alkyl derivatives.[1] Previous studies[2] have suggested that this reaction involves the initial formation of bis(dimethyl sulfide)decaborane(12), which can then dissociate a dimethyl sulfide, yielding a reactive $B_{10}H_{12}SMe_2$ species. Further reaction of this $B_{10}H_{12}SMe_2$ intermediate with the alkyne then leads to the direct insertion of the two-carbon acetylenic unit into the cage along with dissociation of the remaining SMe_2 and H_2 loss to yield the final product.

We have now investigated the dimethyl sulfide promoted reactions of decaborane(14) with two silylated acetylenes, bis(trimethylsilyl)acetylene and (trimethylsilyl)propyne, and report that, in contrast to the results discussed above,

---

(1) (a) Kutal, C. R.; Owen, D. A.; Todd, L. J. *Inorg. Synth.* **1968**, *11*, 19–23. (b) Heying, T. L.; Ager, J. W., Jr.; Clark, S. L.; Mangold, D. L.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089–92. (c) Fein, M. M.; Grafstein, D.; Paustian, J. E.; Bobinski, J.; Lichstein, B. M.; Mayes, N.; Schwartz, N. N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1115–19. (d) Zakharkin, L. I.; Stanko, V. I.; Brattsev, V. A.; Chapovskii, Yu. A.; Klimova, A. I.; Oxlobystin, O. Yu.; Ponomarenko, A. A. *Dokl. Akad. Nauk SSSR* **1964**, *155*, 1119–22. (e) Dupont, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1643. (f) Paxson, T. E.; Callahan, K. P.; Hawthorne, M. F. *Inorg. Chem.* **1973**, *12*, 708–9. (g) Fein, M. M.; Bobinski, J.; Mayes, N.; Schwartz, N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1111–15.

(2) Hill, W. E.; Johnson, F. A.; Novak, R. W. *Inorg. Chem.* **1975**, *14*, 1244–49.