

# Synthetic and Mechanistic Aspects of Intramolecular Aliphatic CH Bond Activation by Ti(IV) and Zr(IV) Metal Centers

Stanley L. Latesky,<sup>†</sup> Anne K. McMullen,<sup>†</sup> Ian P. Rothwell,<sup>\*†</sup> and John C. Huffman<sup>‡</sup>

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. Received February 11, 1985

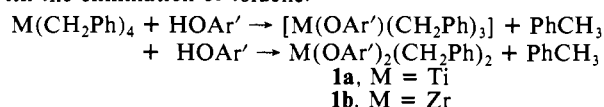
**Abstract:** The complexes  $M(\text{OAr}')_2(\text{CH}_2\text{Ph})_2$  ( $\text{OAr}' = 2,6\text{-di-}t\text{-butylphenoxide}$ ;  $M = \text{Ti, Zr}$ ) undergo the loss of 1 equiv of toluene on mild thermolysis and formation of a monometalated complex  $M(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{Ph})$ , in which one of the CH bonds of a *tert*-butyl group has been activated and cleaved. Addition of 2,6-di-*tert*-butylphenol ( $\text{HOAr}'$ ) to this complex yields  $M(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')_2$  and 1 equiv of toluene while pyridine gives the adducts  $M(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{Ph})(\text{py})$  as yellow ( $M = \text{Ti}$ ) and white ( $M = \text{Zr}$ ) powders. Although these complexes were found unsuitable for crystallographic study, the related compound  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{SiMe}_3)(\text{py})$  has been isolated and a single-crystal X-ray diffraction study has confirmed the presence of the six-membered metallocycle. The molecule is found to adopt a pseudo-*tbp* geometry in the solid state with the pyridine nitrogen atom and the oxygen atom of the cyclometalated aryl oxide occupying the axial sites. The unmetalated aryl oxide oxygen atom and two carbon atoms form the equatorial plane. Crystal data for  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{SiMe}_3)(\text{py})$  at  $-165^\circ\text{C}$  follow:  $a = 18.837(8)\text{ \AA}$ ,  $b = 17.823(6)\text{ \AA}$ ,  $c = 10.923(3)\text{ \AA}$ ,  $\beta = 99.62(1)^\circ$ ,  $Z = 4$ ,  $d_{\text{calcd}} = 1.146\text{ g cm}^{-3}$  in space group  $P2_1/a$ . Of the 4734 unique intensities collected with  $\text{Mo K}\alpha$  the 3372 with  $F_o > 2.33\delta(F)$  were used in the least-squares refinement to give residuals  $R(F) = 0.0662$  and  $R_w(F) = 0.0624$ . Kinetic measurements of the cyclometalation step showed the reaction to be unimolecular with the following activation parameters for  $M = \text{Ti}(\text{Zr})$ :  $\Delta H^\ddagger = 23.0(21.6)\text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -13(-19)\text{ eu}$ . These data are argued to be consistent with those for a multicenter transition state for the activation of the CH bonds at these  $d^0$  metal centers. The reaction has also been shown to be only slightly sensitive to substituents on the benzyl leaving group. The possible mechanistic implications of these data are discussed.

The activation of normally inert CH bonds, either intra- or intermolecularly, by homogeneous transition-metal systems has been an area of intense research effort.<sup>1</sup> Early systems that were developed typically involved later transition metals and were characterized by a mechanistic similarity, i.e., the use of an oxidative-addition step for the activation of the particular CH bond in question.<sup>2</sup> More recent work has shown that oxidative addition of even hydrocarbon CH bonds is possible to electron rich, coordinatively unsaturated metal centers generated either photochemically or thermally.<sup>3</sup> Over the last 5 years a number of reactions have been characterized where the relatively mild activation of CH bonds occurs at a  $d^0$  metal center, a situation that effectively rules out direct activation of the CH bond by oxidative addition.<sup>4</sup> Recent findings by Watson<sup>5</sup> and Marks<sup>6</sup> have shown that activation of even methane is possible at  $\text{Lu}^{3+}$  and  $\text{Th}^{4+}$  metal centers, respectively.

We at Purdue recently reported our observations concerning the intramolecular activation (cyclometalation) of the aliphatic CH bonds in 2,6-di-*tert*-butylphenol on Ta(V) centers.<sup>7</sup> Studies have allowed us to implicate not only alkyl groups but also alkylidene<sup>8</sup> and benzyne (*o*-phenylene)<sup>9</sup> functions for the activation of CH bonds in this ligand. We have now extended our studies of the metalation of this ligand to the group 4 metals Ti and Zr and developed systems that allow not only synthetic but also accurate kinetic studies of the CH bond activation step to be made. This paper reports these findings and also mechanistic conclusions for the activation of the CH bonds at these  $d^0$  metal centers.

## Synthesis and Characterization of Compounds

The addition of 2,6-di-*tert*-butylphenol ( $\text{HOAr}'$ ) to the tetra-benzyls of titanium or zirconium,  $M(\text{CH}_2\text{Ph})_4$  ( $M = \text{Ti, Zr}$ ), leads to the stepwise substitution of one and then two benzyl groups with the elimination of toluene.<sup>10</sup>



In the case of titanium only the bis-substitution product has been isolated, while for zirconium both the tris- and bis-benzyl

complexes have been obtained and extensively characterized both by nuclear magnetic resonance and by single-crystal X-ray diffraction studies.<sup>10</sup> The compounds of relevance to this particular study are the bis-benzyl complexes, deep-red (**1a**) and light yellow (**1b**). The solid-state-structure analysis of **1b** has shown it to be a discrete, mononuclear system with no aryloxy bridges, and we conclude that both **1a** and **1b** are isostructural on the basis of spectroscopic data.

On careful thermolysis in hydrocarbon solvents, typically toluene at  $120^\circ\text{C}$ , compounds **1a,b** generate 1 equiv of toluene and a single new species (**2a,b**). Monitoring these reactions by  $^1\text{H NMR}$  shows a clean, essentially quantitative conversion of **1a,b** to **2a,b**. In the case of **1a** this reaction is found to occur even at  $25^\circ\text{C}$  over a period of weeks. On the basis of NMR and mass spectral studies we assign **2a,b** a mononuclear structure in which the metalation

(1) (a) Shilov, A. E. "Activation of Saturated Hydrocarbons by Transition Metal Complexes"; Kluwer Academic Publishers: New York, 1984. (b) Parshall, G. W. *Catalysis* **1977**, *1*, 335. (c) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (d) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97. (e) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (f) Dehand, J.; Pfeiffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (g) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113; **1970**, *3*, 139.

(2) (a) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. (b) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27. (c) Parshall, G. W. "Homogeneous Catalysis"; John Wiley and Sons: New York, 1980.

(3) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (b) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 2563. (c) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.

(4) (a) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (b) Bercaw, J. E. *Pure Appl. Chem.* **1984**, *1*.

(5) (a) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214. (b) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357.

(6) (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (b) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (c) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.

(7) (a) Chamberlain, L.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1984**, *106*, 1847. (b) Chamberlain, L.; Keddington, J.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1982**, *1*, 1538.

(8) Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 7338.

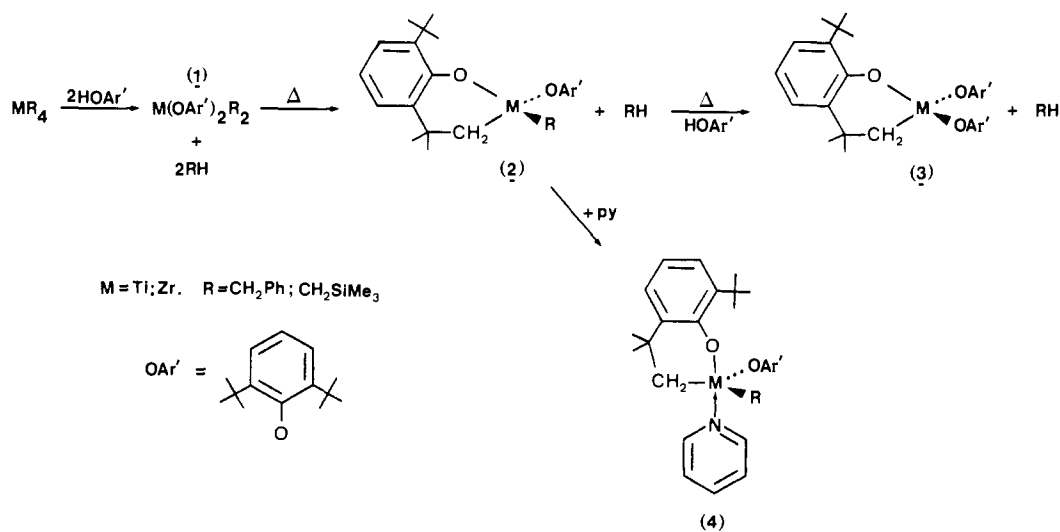
(9) Chamberlain, L.; Rothwell, I. P. *J. Am. Chem. Soc.* **1983**, *105*, 1665.

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

<sup>†</sup>Purdue University.

<sup>‡</sup>Indiana University.

## Scheme I



of one of the *tert*-butyl CH bonds of an aryloxide ligand has taken place with the elimination of 1 equiv of toluene (Scheme I). The approximately tetrahedral geometry about the metal atoms expected in the mono-metalated compounds **2** can be seen to result in both the benzyl ( $\text{PhCH}_2$ ) and metalated ( $\text{CMe}_2\text{CH}_2$ ) methylene protons becoming diastereotopic. In the  $^1\text{H}$  NMR of both **2a** and **2b** the resulting AB patterns can be readily resolved and furthermore easily distinguished by the smaller value of  $^2J(\text{H}_\text{A}\text{CH}_\text{B})$  for the benzyl protons. The lack of a plane of symmetry through the cyclometalated chelate ring also results in a nonequivalence for the  $\text{CMe}_2\text{CH}_2$  methyl groups, causing them to resonate at different frequencies in the  $^1\text{H}$  NMR spectrum. The presence of the metalated chelate is also confirmed by the  $^{13}\text{C}$  NMR spectra of **2** which appear qualitatively similar. The most dramatic effect is a large downfield shift of the metalated carbon,  $\text{M}-\text{CH}_2\text{CMe}_2$ , to  $\delta$  116.5 (**2a**) and  $\delta$  78.4 (**2b**) while the  $\alpha$ -carbon of the remaining benzyl ligand is seen at  $\delta$  87.3 and 63.0, respectively. A downward shift of the  $\text{M}-\text{CH}_2\text{CMe}_2$  carbon is also evident along with nonequivalent  $\text{M}-\text{CH}_2\text{CMe}_2$  carbon resonances. The downfield shifts of the carbon atoms contained in chelated rings compared to their expected nonchelating positions have been noted in a number of cyclometalated compounds,<sup>11</sup> and the dramatic effect chelate rings can have on chemical shifts of phosphorous nuclei in the ring has been noted previously.<sup>12</sup>

The monometalated compounds can be readily isolated after thermolysis of **1** by removal of solvent to yield light red (**2a**) and pale yellow (**2b**) oils. All attempts to obtain crystalline samples of these compounds have so far failed.

Although the spectroscopic details of **2a** and **2b** are qualitatively similar, some significant quantitative differences exist. In particular the resonances due to the metalated methylene protons of **2b**,  $\text{Zr}-\text{CH}_2\text{CMe}_2$ , appear at unusually high field ( $\delta$  -0.41 and +1.08; both doublets) compared to  $\delta$  2.54 and 1.78 in the titanium analogue (**2a**). Furthermore, a slightly high field shift of the ortho protons of the benzyl ligand in **2b** at 6.44 ppm contrasts with a normal shift for this group in **2a**. We interpret these differences as being due to the presence of considerable  $\pi$  interaction between the zirconium metal and the aromatic ring of the benzyl group in **2b** compared to a purely  $\sigma$ -bound benzyl in **2a**. This type of multisite interaction to benzyl groups has been structurally characterized in the homoleptic compounds  $\text{M}(\text{CH}_2\text{Ph})_4$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ )<sup>13</sup> as well as the compound  $\text{Zr}(\text{OAr}')(\text{CH}_2\text{Ph})_3$ .<sup>10</sup> Similar actinide-benzyl interactions have also been characterized.<sup>14</sup>

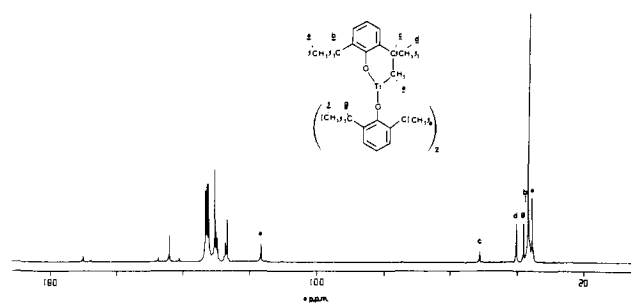


Figure 1.  $[\text{H}]^{13}\text{C}$  NMR spectrum of  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')_2$  (**3a**).

A characteristic of this type of interaction is the upfield shift of the ortho protons of the benzyl groups. A reasonable rationalization for the presence of a multisite or partially  $\pi$ -bound benzyl group in **2b** compared to a "normal"  $\sigma$ -bound group in **2a** is the significantly smaller coordination sphere in the latter compound (vide infra) sterically not allowing the metal to interact with the benzyl  $\pi$  cloud.

Although the nonmetalated compounds **1** will not react further with 2,6-di-*tert*-butylphenol ( $\text{HOAr}'$ ), the cyclometalated compounds will react on warming to eliminate another equivalent of toluene to form the monometalated, bis-aryloxides  $\text{M}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')_2$  ( $\text{M} = \text{Ti}$ , **3a**;  $\text{M} = \text{Zr}$ , **3b**) as yellow and off-white crystalline solids, respectively (Scheme I). The presence of a plane of symmetry through the chelate ring in **3** now greatly simplifies the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra compared to **2** (Figure 1). The metalated  $\text{M}-\text{CH}_2$  protons and  $\text{M}-\text{CH}_2\text{CMe}_2$  methyl groups are now equivalent and give rise to singlets in the  $^1\text{H}$  NMR spectrum, while the metalated carbon  $\text{M}-\text{CH}_2\text{CMe}_2$  is still present at  $\delta$  111.7 and 83.1. Furthermore, the removal of the benzyl group makes the spectra of **3a** and **3b** much more comparable as identical structures are now presumably adopted.

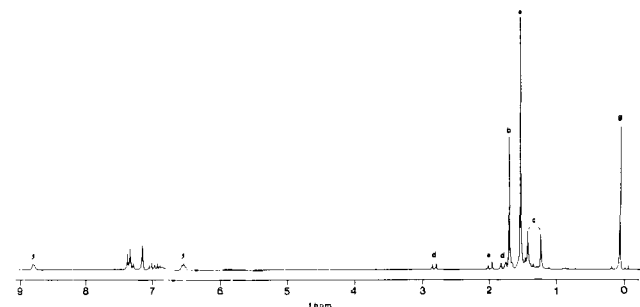
Monometalated complexes **2** also readily react with pyridine in solution to form sparingly soluble yellow crystalline adducts  $\text{M}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{py})(\text{CH}_2\text{Ph})$  ( $\text{M} = \text{Ti}$ , **4a**;  $\text{M} = \text{Zr}$ , **4b**). The  $^1\text{H}$  NMR spectra of these adducts are comparable and indicate that differences due to the  $\pi$  interaction present in the zirconium complex **2b** have now gone. Clearly a number of isomers are possible for these five-coordinate adducts. Unfortunately, suitable crystals of **4a** or **4b** were not obtained for X-ray analysis. However, crystals of an analogous, presumably isostructural, molecule were obtained in the following study.

(11) Deeming, A. J.; Rothwell, I. P. *Pure Appl. Chem.* **1980**, *52*, 649 and references therein.

(12) Garrou, P. *Chem. Rev.* **1981**, *81*, 229.

(13) (a) Davis, G. R.; Jarvis, J. A. J.; Kilbourn, B. T.; Piols, A. J. P. *J. Chem. Soc., Chem. Commun.* **1971**, 677. (b) Davis, G. R.; Jarvis, J. A. J.; Kilbourn, B. T. *J. Chem. Soc., Chem. Commun.* **1971**, 1511.

(14) (a) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W., *J. Am. Chem. Soc.* **1982**, *104*, 4692. (b) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293.



**Figure 2.**  $^1\text{H}$  NMR (200 MHz) spectrum of  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{SiMe}_3)(\text{py})$  (**4c**). Signals indicated belong to (a)  $\text{OC}_6\text{H}_3\text{Bu}'_2$ , (b)  $\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2$ , (c)  $\text{OC}_6\text{H}_3\text{CMe}_2\text{CH}_2$ , (d)  $\text{CH}_2\text{SiMe}_3$ , (e)  $\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2$ , and (f)  $\text{C}_3\text{H}_5\text{N}$ .

**Table I.** Crystallographic Data for  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{SiMe}_3)(\text{py})$  (**4c**)

formula	$\text{TiSiO}_2\text{NC}_{37}\text{H}_{57}$
fw	623.85
space group	$P2_1/a$
$a$ , Å	18.837 (8)
$b$ , Å	17.823 (6)
$c$ , Å	10.923 (3)
$\beta$ , deg	99.62 (1)
$Z$	4
$V$ , Å <sup>3</sup>	3615.8
density (calcd), g/cm <sup>3</sup>	1.146
crystal size, mm	0.23 × 0.23 × 0.27
crystal color	yellow
radiation	$\text{Mo K}\alpha$ ( $\gamma = 0.71069$ Å)
linear abs coeff, cm <sup>-1</sup>	2.947
temp, °C	-165
detector aperture	3.0 mm wide × 4.0 mm high, 22.5 cm from crystal
sample to source distance, cm	23.5
takeoff angle, deg	2.0
scan speed, deg/min	4.0
scan width, deg	$2.0 \pm 0.692 \tan \theta$
bkgd counts, s	10
$2\theta$ range, deg	6-45
data collected	5517
unique data	4734
unique data with $F_o > 2.33 \sigma(F)$	3372
$R(F)$	0.0662
$Rw(F)$	0.0624
goodness of fit	1.103
largest $\delta/\sigma$	0.05

Attempts to substitute  $\text{Ar}'\text{OH}$  into the coordination sphere of  $\text{Ti}(\text{CH}_2\text{SiMe}_3)_4$  proved difficult, no reaction being observed at 25 °C over days. However, on warming to 80 °C a mixture of the bulky phenol and the tetraalkyl did react to generate  $\text{Me}_4\text{Si}$  and a yellow oil. Analysis of this oil by  $^1\text{H}$  NMR showed a mixture of products the majority of which could, on the basis of the benzyl work, be identified. The major component was identified as  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{SiMe}_3)$  (**2c**), along with NMR signals corresponding to authentic samples of  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')_2$  (**3a**) and free  $\text{HOAr}'$ . Addition of pyridine to hexane solutions of this crude oil resulted in the slow deposition at room temperature of yellow crystals of the adduct  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{py})(\text{CH}_2\text{SiMe}_3)$  (**4c**). The  $^1\text{H}$  NMR spectra of this pyridine adduct are identical with those of the benzyl complex (**4a**) except for the differing alkyl resonances (Figure 2). From this reactivity study we conclude that the rate of substitution of the alkyl groups in  $\text{Ti}(\text{CH}_2\text{SiMe}_3)_4$  is comparable to the rate of metalation in the alkyl aryloxides thus formed. Whether metalation occurs in a complex of formula  $\text{Ti}(\text{OAr}')(\text{CH}_2\text{SiMe}_3)_3$  or  $\text{Ti}(\text{OAr}')_2(\text{CH}_2\text{SiMe}_3)_2$  is unknown.

#### Solid-State Structure of $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{py})(\text{CH}_2\text{SiMe}_3)$

A single-crystal X-ray diffraction study was carried out on complex **4c** to both confirm and characterize the six-membered

**Table II.** Fractional Coordinates and Isotropic Thermal Parameters for  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{SiMe}_3)(\text{py})$  (**4c**)

atom	$10^4x$	$10^4y$	$10^4z$	$10^3\beta_{\text{iso}}$
Ti(1)	7792.1 (5)	1607 (1)	2282 (1)	18
C(2)	8193 (3)	2030 (3)	4090 (5)	28
Si(3)	8849 (1)	1587 (1)	5347 (1)	26
C(4)	9060 (4)	589 (4)	5050 (7)	45
C(5)	8505 (4)	1633 (5)	6854 (6)	46
C(6)	9721 (3)	2103 (4)	5563 (6)	33
N(7)	8406 (2)	2543 (3)	1468 (4)	23
C(8)	8104 (3)	2939 (3)	452 (5)	26
C(9)	8468 (3)	3486 (3)	-74 (6)	31
C(10)	9166 (3)	3657 (3)	442 (6)	33
C(11)	9479 (3)	3269 (4)	1490 (6)	34
C(12)	9087 (3)	2717 (3)	1979 (6)	28
O(13)	7461 (2)	724 (2)	2784 (4)	25
C(14)	7560 (3)	-36 (3)	2866 (5)	20
C(15)	8100 (3)	-353 (3)	2272 (5)	26
C(16)	8198 (3)	-1131 (3)	2397 (6)	31
C(17)	7783 (4)	-1550 (4)	3075 (6)	36
C(18)	7255 (4)	-1226 (3)	3623 (5)	31
C(19)	7124 (3)	-455 (3)	3530 (5)	26
C(20)	8543 (3)	71 (3)	1445 (6)	26
C(21)	8552 (3)	942 (3)	1589 (6)	25
C(22)	8207 (3)	-109 (4)	91 (6)	33
C(23)	9322 (4)	-187 (4)	1654 (7)	44
C(24)	6526 (3)	-91 (3)	4138 (5)	27
C(25)	6872 (3)	461 (4)	5149 (5)	32
C(26)	5976 (3)	319 (4)	3173 (6)	32
C(27)	6117 (3)	-670 (4)	4780 (6)	36
O(28)	6952 (2)	2011 (2)	1410 (3)	20
C(29)	6332 (3)	2333 (3)	830 (5)	19
C(30)	5995 (3)	2049 (3)	-343 (5)	24
C(31)	5394 (3)	2430 (4)	9064 (5)	31
C(32)	5105 (3)	3037 (4)	-427 (6)	32
C(33)	5421 (3)	3279 (3)	752 (5)	26
C(34)	6022 (3)	2937 (3)	1403 (5)	21
C(35)	6259 (3)	1343 (3)	-937 (5)	25
C(36)	5763 (4)	1136 (4)	-2162 (6)	40
C(37)	7014 (3)	1446 (4)	-1259 (6)	33
C(38)	6252 (3)	667 (3)	-80 (6)	29
C(39)	6319 (3)	3198 (3)	2740 (5)	23
C(40)	7074 (3)	3531 (3)	2835 (5)	24
C(41)	6293 (3)	2540 (3)	3641 (5)	25
C(42)	5854 (4)	3819 (4)	3172 (6)	35

**Table III.** Selected Bond Distances and Angles for  $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}'\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{SiMe}_3)(\text{py})$  (**4c**)

Ti-O(13)	1.810 (4)	Ti-C(2)	2.131 (6)
Ti-O(28)	1.850 (4)	Ti-C(21)	2.095 (6)
Ti-N(7)	2.293 (5)		
O(13)-Ti-O(28)	100.7 (2)	N(7)-Ti-C(2)	88.7 (2)
O(13)-Ti-N(7)	166.3 (2)	N(7)-Ti-C(21)	81.5 (2)
O(13)-Ti-C(2)	96.6 (2)	C(2)-Ti-C(21)	112.2 (2)
O(13)-Ti-C(21)	84.8 (2)	Ti-O(13)-C(14)	146.1 (4)
O(28)-Ti-N(7)	87.7 (2)	Ti-O(28)-C(29)	176.6 (3)
O(28)-Ti-C(2)	118.7 (2)	Ti-C(2)-Si(3)	128.4 (3)
O(28)-Ti-C(21)	127.7 (2)	Ti-C(21)-C(20)	127.1 (4)

chelate and also to identify the one isomer adopted out of the many possibilities. A total of 12 isomers can be seen for square-pyramidal geometry and nine for a trigonal bipyramid. Furthermore,  $^1\text{H}$  NMR cannot rule out any one as each would give rise to an AB system for the  $\text{Ti}-\text{CH}_2\text{CMe}_2$  group; i.e., each of the 21 diastereoisomers exists as an enantiomeric pair giving rise to 42 overall possible isomers for the molecule.

An ORTEP view of the molecule is given in Figure 3 along with the numbering scheme. A view emphasizing the chelate ring and metal geometry in the very crowded molecule is shown in Figure 4. Table I gives the crystallographic data while Table II gives the fractional coordinates and isotropic thermal parameters. Some important bond lengths and angles are given in Table III. It can be seen that the molecule adopts what is best described as an approximate trigonal-bipyramidal geometry with the chelate oxygen occupying an axial site trans to the pyridine nitrogen. The

Table IV. Kinetic Data and Activational Parameters<sup>a</sup>

complex	$T/^\circ\text{C}$	$10^5 k/s^{-1}$	$E_a$	$\log A$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
Ti(OAr') <sub>2</sub> (CH <sub>2</sub> Ph) <sub>2</sub>	73	3.19	23.6 ± 1.0	10.5 ± 1	23.0 ± 1.0	-13 ± 3
	85	11.3				
	95	26.5				
	105	60.9				
	114	126.0				
Zr(OAr') <sub>2</sub> (CH <sub>2</sub> Ph) <sub>2</sub>	95	7.12	22.4 ± 1.0	9.1 ± 1	21.6 ± 1.0	-19 ± 3
	105	15.0				
	114	32.3				
	130	99.6				
Zr(OAr') <sub>2</sub> (CH <sub>2</sub> Ph-4Me) <sub>2</sub>	114	39.2				
Zr(OAr') <sub>2</sub> (CH <sub>2</sub> Ph-4F) <sub>2</sub>	114	45.8				
Zr(OAr') <sub>2</sub> (CH <sub>2</sub> Ph-3F) <sub>2</sub>	114	18.4				

<sup>a</sup>  $E_a$  and  $\Delta H^\ddagger$  in kcal mol<sup>-1</sup>;  $\Delta S^\ddagger$  in entropy units.

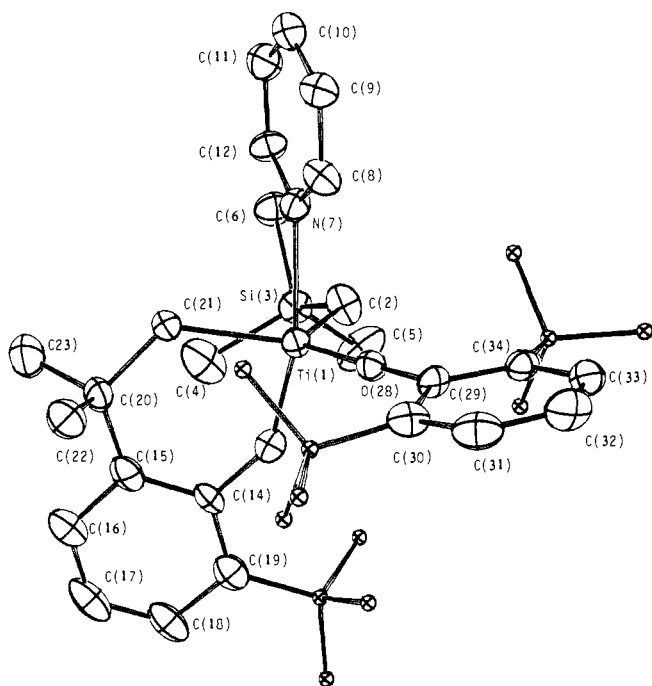


Figure 3. ORTEP view of Ti(OC<sub>6</sub>H<sub>3</sub>Bu'CMMe<sub>2</sub>CH<sub>2</sub>)(OAr')(CH<sub>2</sub>SiMe<sub>3</sub>)(py) (**4c**). In order to simplify the picture the nonmetalated Bu' ellipsoids have been decreased.

equatorial plane then consists of the metalated alkyl carbon atom, nonmetalated aryloxy oxygen atom, and nonmetalated alkyl carbon atom. The distortions from true *tbp* angles are not unexpected given the differing steric demands of the ligands. However, some aspects of the structure are worthy of note. The Ti–O distances of 1.810 (4) and 1.850 (4) Å are short, implying considerable amounts of oxygen  $p$  to titanium  $d$   $\pi$  bonding although slightly longer than the distances of 1.79 (2) and 1.78 (1) Å found in the compounds Ti(OAr')<sub>3</sub><sup>15</sup> and Ti(OAr'')<sub>4</sub> (OAr'' = 2,6-diisopropylphenoxide). The Ti–O–Ar' angle of 176.6° to the nonmetalated aryloxy is also consistent with the presence of Ti–O multiple bonding, but it is also very characteristic of these bulk phenoxides coordinated to early transition metals.<sup>15</sup> The six-membered metalocycle resulting from the cyclometalation can be seen to readily accommodate an angle at the metal of 84.8° with little puckering. The reason for this comfortable situation again relates to the wide Ti–O–C angle of 146.1° inside the chelate which tends to flatten the metalocycle. The only noticeable puckering in the six-membered ring from planarity occurs at the CH<sub>2</sub>CMe<sub>2</sub> carbon atoms, allowing an almost perfectly staggered conformation for the hydrogen and methyl substituents on looking down this C–C axis. Hence the six-membered cyclometalated ring can easily accommodate two *cis*-coordination sites. A similar conformation of this particular chelate was observed in the

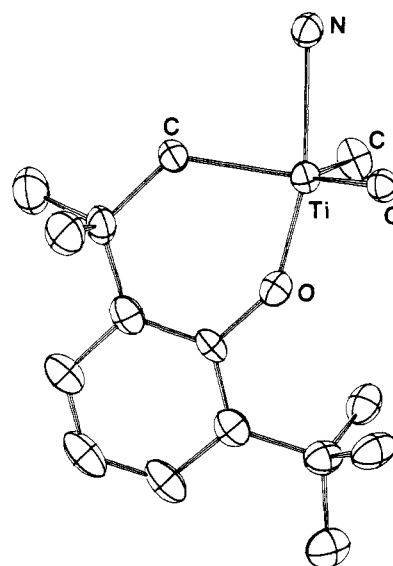


Figure 4. ORTEP view of (**4c**) emphasizing the coordination about the titanium atom and the cyclometalated chelate.

structurally related complex Ta(OC<sub>6</sub>H<sub>3</sub>Bu'CMMe<sub>2</sub>CH<sub>2</sub>)(OAr')(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> where yet again a *tbp* geometry was adopted, but this time with *trans*-axial oxygen atoms.<sup>7</sup>

#### Kinetic Studies of the Cyclometalation Reaction

Given the quantitative transformation of **1** to **2** on thermolysis in hydrocarbon solvents, we have studied the kinetics of the ring-closure reaction for the two metals titanium and zirconium. Although a definite lightening of color was observed on cyclometalation—from deep-red to orange for **1a** and from yellow to almost colorless for **1b**—it was decided to monitor the thermal disappearance of **1** by <sup>1</sup>H NMR rather than electronic absorption spectroscopy. Samples for this study were dissolved in toluene-*d*<sub>8</sub> in 5-mm NMR tubes and the tubes sealed under vacuum. Thermolysis was then carried out by *total* submersion of the NMR tube in a constant temperature oil bath (±1 °C) for varying amounts of time. The tube was then removed and rapidly cooled before NMR spectra were obtained at the probe temperature of 35 °C. The extent of reaction was obtained by two methods. The first involved observing the decrease in the M–CH<sub>2</sub>Ph singlet intensity under roughly identical machine conditions of resolution as judged by using the *pentet* of the protio impurity in commercial toluene-*d*<sub>8</sub>. The second method was to compare the intensity of the product and initial unmetalated complex signals to determine the fraction converted. Both methods yielded almost identical results.

Our results indicate that the cyclometalation of both **1a** and **1b** follows first-order kinetics, consistent with a unimolecular activation step (*vide infra*) (Figure 5). The first-order rate constants for the two metal systems at various temperatures are given in Table IV. The use of either Arrhenius or activated complex theories allows the activation parameters in Table IV to be obtained. Plots of  $\ln(k/T)$  vs.  $T^{-1}$  (K<sup>-1</sup>) are given for both

(15) Latesky, S.; Keddington, J.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995.

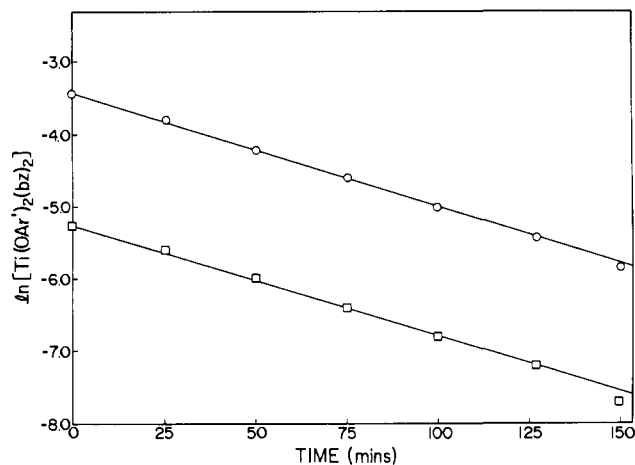


Figure 5. First-order plot for the disappearance of  $\text{Ti}(\text{OAr}')_2(\text{CH}_2\text{Ph})_2$  (**1a**) at 95 °C in toluene- $d_8$ .

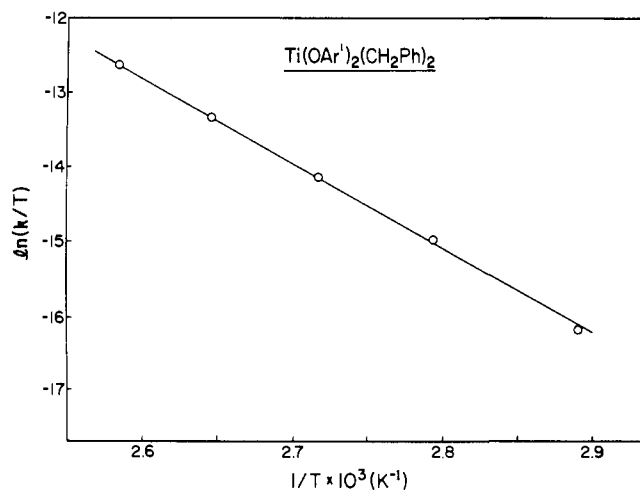


Figure 6. Activated complex theory plot for the cyclometalation of  $\text{Ti}(\text{OAr}')_2(\text{CH}_2\text{Ph})_2$  (**1a**).

$M = \text{Ti}$  (**1a**) and  $\text{Zr}$  (**1b**) (Figures 6 and 7).

### Mechanistic Considerations

The mechanism of CH bond activation at these  $d^0$  metal centers is of obvious interest, especially as the number of such reactions has increased rapidly over the last few years.<sup>4-6</sup> The most plausible mechanistic pathways can be accommodated into two distinct areas. The first involves a homolytic or radical pathway in which the breaking of the metal-benzyl bond occurs in the activation step to generate a benzyl radical, presumably caged, which then carries out a hydrogen atom abstraction from one of the *tert*-butyl groups of an aryloxy ligand followed by ring closure to the product. The second, and by far most popular in the literature, envisages a multicenter transition state in which the new M-C bond is being formed at the same time that the leaving group-metal bond is being broken.<sup>16</sup> This pathway allows the reaction to occur with no change in metal oxidation state throughout the course of the reaction.

The data we have obtained, Table IV, are much more consistent with a multicenter pathway than a radical initiation for the following reasons. Although it can be seen that the titanium system undergoes more facile cyclometalation than the zirconium analogue, the difference in rates is only small. Of particular importance is the negligible difference in the enthalpies of acti-

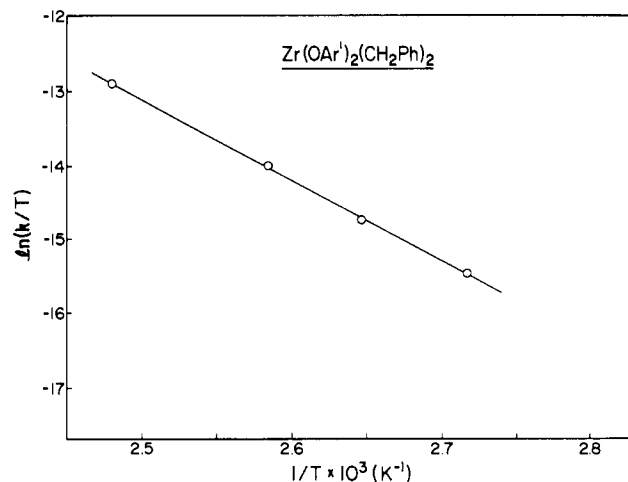


Figure 7. Activated complex theory plot for the cyclometalation of  $\text{Zr}(\text{OAr}')_2(\text{CH}_2\text{Ph})_2$  (**1b**).

vation ( $\Delta H^\ddagger$ ) for the two processes. A typical feature of the chemistry of the early transition metals is a significant increase in the values of mean bond dissociation energies on going from first-row d-block elements to their second-row analogues.<sup>17</sup> In the case of the homoleptic benzyls the value of  $D(\text{M}-\text{CH}_2\text{Ph})$  has been measured as 49 kcal mol<sup>-1</sup> for  $M = \text{Ti}$  and 60 kcal mol<sup>-1</sup> for  $M = \text{Zr}$ .<sup>18</sup> A similar trend is seen for the methyl and neopentyl derivatives. Hence, one would expect to see a difference in  $\Delta H^\ddagger$  for the two reactions if homolytic cleavage of the benzyl bond was the activation step. The similarity of  $\Delta H^\ddagger$  can be accommodated into a multicenter pathway in which one is both forming and breaking carbon bonds to the same metal center. Further strong support for the four-center pathway comes from the moderately large and negative entropy of activation ( $\Delta S^\ddagger$ ) consistent with the achievement of a fairly ordered transition state during the activation step. Similar values of  $\Delta S^\ddagger$  have been seen for the ring closure of  $\text{CH}_2\text{CMe}_3$  and  $\text{CH}_2\text{SiMe}_3$  groups on thorium and attributed to an analogous transition state.<sup>6</sup> Although the rate of metalation at titanium is faster than at zirconium, analysis of the data shows that this rate difference is, if anything, entropically based. This can be rationalized in terms of the relative sizes of the coordination spheres of the two metals. The covalent radius of titanium is normally considered to be 0.14 Å smaller than that of zirconium. Hence, the coordination sphere is more crowded in the titanium case and hence presumably less freedom of motion of the aryloxy ligands will be present in the ground state. Slightly less entropy will, therefore, be lost on going to the four-center transition state. Measurement of the activation energy of the restricted rotation of aryloxy groups in the compounds  $\text{M}(\text{OAr}')_3\text{Cl}$  ( $M = \text{Ti}, \text{Zr}, \text{Hf}$ ) shows values of 12.3, 10.7, and 10.8 kcal mol<sup>-1</sup>,<sup>15</sup> consistent with this picture of a more crowded coordination sphere for titanium. Similar, moderately large negative entropies of activation have been reported by Marks for the related cyclometalation of alkyl groups on Th(IV) and U(IV) metal centers<sup>19</sup> and contrast with the large positive values of  $\Delta S^\ddagger$  reported by Whitesides for analogous reactions on Pt(II).<sup>20</sup> This latter observation was explained in terms of a rate-determining reductive elimination of alkane following an oxidative addition of a CH bond.

It is interesting to contrast this behavior observed for these aryloxy systems with that reported by Andersen et al. for the compounds  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2\text{R}_2$  ( $M = \text{Zr}, \text{Hf}; \text{R} = \text{CH}_3$ ) where thermolysis leads to a dinuclear complex in which activation (cyclometalation) of the  $\gamma$ -CH bonds of the amido ligands has

(17) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

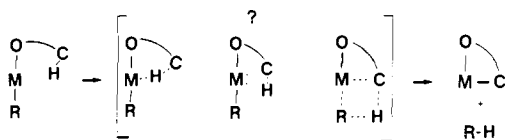
(18) Lappert, M. F.; Patil, D. S.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830.

(19) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357.

(20) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124.

(16) Intermolecular hydrogenolysis of early transition metal alkyls has been shown to occur by a related mechanism, see: (a) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246. (b) Mayer, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157. (c) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008.

Scheme II



taken place.<sup>21</sup> In the case of  $M = \text{Ti}$ , no such metalation reaction is seen. This was explained by the steric inhibition of the reaction caused by the more crowded coordination sphere of titanium not allowing the CH bond access to the metal center for activation.<sup>21</sup> Hence, steric effects may either enhance or retard such reactions.

We have attempted to gain more insight into the so far ill-defined electronic nature of the transition state of these reactions by making use of substituent effects in the benzyl leaving group. We have isolated zirconium complexes containing 4-F, 3-F, and 4-Me substituents in the benzyl groups using essentially identical procedures to those for the unsubstituted complex. Kinetic data (114 °C) for the cyclometalation in these complexes are collected in Table IV. Unfortunately, we have been unable to isolate pure samples of the compounds containing other substituents such as 4-OMe and 4-CF<sub>3</sub> due to the as yet unexplained high thermal instability of the homoleptic complexes. It can be seen that there is only a small substituent effect on the rate of these reactions.

Interpretation of these rate differences in terms of the transition-state structure is not straightforward, as there appears to be no systematic correlation with the known  $\sigma$  values of these substituents. Over the last 10 years a body of literature has accumulated dealing with the characterization of ground-state interactions between CH bonds and electron-deficient transition-metal complexes.<sup>22</sup> In particular, recent work by Green has shown that significant interactions between either  $\alpha$ - or  $\beta$ -CH bonds of alkyl ligands can occur to a Ti(IV) metal center.<sup>23</sup> Structural data indicating a ground-state Yb...CH interaction have been reported by Andersen.<sup>24</sup> In this case the metal appears to be interacting directly with the carbon atom of a methyl group in the ligand N(SiMe<sub>3</sub>)<sub>2</sub>. This ligand is known to undergo activation of these CH bonds in other metal systems. Such an interaction may be an important point (possibly even an intermediate) on the reaction coordinate leading to the activation of CH bonds on such metals. Such interactions can be considered from the point of view of two extreme cases: i.e., a linear or side-on three-center, two-electron bond. Examples of both situations have been documented.<sup>22</sup> For the case of the carbon-hydrogen bonds of the Bu<sup>t</sup> groups of 2,6-di-*tert*-butylphenoxide (OAr'), molecular models indicate that it is very difficult to set up a situation that allows the CH bond to approach a metal to which the OAr' is bound in a side-on fashion. Instead an end-on or linear interaction seems to be the most favorable conformation, assuming no large deformations of the skeletal backbone. However, one can then imagine that the linear interaction could then lead to a side-on bonding mode with the metal now interacting directly with the carbon and hydrogen atoms (Scheme II). The removal of electron density from the CH bond by such an interaction would be expected to lead to significant proton character for the hydrogen atom. One could envisage a situation where total removal of electron density from the CH bond could lead to a free proton and an alkyl metalate complex. The overall sequence, although very unlikely, would be an SE<sub>2</sub> displacement of proton by the metal center. The substituent data that we have, although minimal, are not consistent with the picture of a proton transfer to the leaving group carbon atom. Instead, the negligible substituent effect is

consistent with the cyclic transition state in which very little charge separation occurs.<sup>25</sup>

## Experimental Section

All operations were performed under a dry nitrogen atmosphere either in a vacuum atmosphere drybox or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone under a nitrogen atmosphere. The tetrabenzyl derivatives of zirconium were synthesized by routine methods from ZrCl<sub>4</sub> (Alfa) and 4 equiv of the corresponding Grignard reagent in diethyl ether. The complexes Zr(OAr')<sub>2</sub>(CH<sub>2</sub>Ph-X)<sub>2</sub> (CH<sub>2</sub>Ph-X = substituted benzyl) were then synthesized by using reported methods.<sup>10</sup> All phenolic reagents were purchased from Aldrich and Co. and were dried before use.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Associates XL-200 spectrometer and referenced to Me<sub>4</sub>Si. Variable-temperature <sup>1</sup>H NMR spectra were obtained on a Perkin-Elmer R32 spectrometer (90 MHz). <sup>1</sup>H NMR of Zr(OAr')<sub>2</sub>(CH<sub>2</sub>Ph-4Me)<sub>2</sub>:  $\delta$  2.71 (s, CH<sub>2</sub>Ph), 1.34 (s, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>'), 6.7-7.3 (m, aromatics). <sup>1</sup>H NMR of Zr(OAr')<sub>2</sub>(CHPh-3F)<sub>2</sub>:  $\delta$  2.71 (s, CHPh), 1.33 (s, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>'), 6.7-7.4 (m, aromatics).

**1. Preparation of Ti(OAr')<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub> (1a).** **A. From Ti(CH<sub>2</sub>Ph)<sub>4</sub>.** To a solution of PhCH<sub>2</sub>MgCl (250 mmol) in diethyl ether (500 mL) was slowly added TiCl<sub>4</sub> (60 mmol) while maintaining the solution temperature below -20 °C. The deep-red suspension was then stirred at this temperature for 2 h. Due to its poor thermal stability, Ti(CH<sub>2</sub>Ph)<sub>4</sub> was not isolated in a pure state from this mixture. However, the mixture was filtered while cold and the resulting intense red ether solution was treated at -20 °C with 2,6-di-*tert*-butylphenol (27 g; 2.2 equiv). The solution was then allowed to warm up to room temperature and stirred for 2 days. The solvent was removed under vacuum and addition of hexane to the resulting red oil followed by cooling gave deep-red microcrystals of the product. The yield was typically 25-40% based on Ti. Anal. Calcd for TiC<sub>42</sub>H<sub>56</sub>O<sub>2</sub>: C, 78.44; H, 9.09. Found: C, 77.35; H, 8.61. <sup>1</sup>H NMR (30 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.25 (s, C<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>'), 3.19 (s, CH<sub>2</sub>Ph), 6.9-7.4 (m, CH<sub>2</sub>Ph and C<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>').

**B. From Ti(OAr')<sub>2</sub>Cl<sub>2</sub>.** The complex Ti(OAr')<sub>2</sub>Cl<sub>2</sub> will react with PhCH<sub>2</sub>MgCl (2 equiv) in diethyl ether to give red solutions of Ti(OAr')<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub> (1a). Workup as above does lead to the product isolated as a red solid, but in much reduced yields. <sup>1</sup>H NMR analysis of the crude product before removal of 1a showed a number of as yet unidentified compounds in solution.

**2. Thermolysis of M(OAr')<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub> (M = Ti, 1a; M = Zr, 1b).** The cyclometalation of these compounds to the monometalated derivatives 2 was achieved by the thermolysis (12 h) of toluene solutions of the compounds sealed in evacuated Pyrex tubes. A constant temperature oil bath (120 °C) was used. The tubes were then taken into the drybox and opened and the solvent removed under vacuum to give essentially quantitative yields of orange 2a and pale yellow 2b as liquids.

Kinetic measurements of this reaction were carried out in sealed, evacuated, 5-mm NMR tubes containing toluene-*d*<sub>8</sub> solutions of either crystalline 1a or 1b. For a number of kinetic runs accurate concentrations of 1 were made up by using various weights of compound dissolved in toluene-*d*<sub>8</sub> in a 5-mL volumetric flask. Once the first-order nature of the reactions had been established, the concentration of complex was not accurately determined in subsequent runs. The sealed tubes were thermolyzed by total immersion into a constant temperature oil bath. After various periods of time, the tubes were removed and cooled rapidly in ice-water before the extent of reaction was determined by <sup>1</sup>H NMR. The rate constant at a particular temperature and activation parameters were determined by using a linear least-squares fitting procedure. **2a:** <sup>1</sup>H NMR (30 °C, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.53 (s, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>'), 1.71 (s, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), 1.13 (s), 1.19 (s, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), 2.54 (d), 1.78 (d, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), 3.08 (d), 2.94 (d, CH<sub>2</sub>Ph), 6.9-7.6 (m, aromatics). **2b:** <sup>1</sup>H NMR (30 °C, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.57 (s, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>'), 1.60 (s, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), 1.42 (s), 1.49 (s, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), -0.41 (d), 1.08 (d, OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), 2.38 (d), 2.57 (d, CH<sub>2</sub>Ph), 6.44 (m, ortho benzyl protons), 6.8-7.6 (m, other aromatics). **2a:** <sup>13</sup>C NMR (30 °C, C<sub>6</sub>D<sub>6</sub>)  $\delta$  87.3 (Ti-CH<sub>2</sub>Ph), 116.5 (Ti-OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), 47.0 (Ti-OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), 35.6, 37.2 (Ti-OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>). **2b:** <sup>13</sup>C NMR (30 °C, C<sub>6</sub>D<sub>6</sub>)  $\delta$  63.0 (Zr-CH<sub>2</sub>Ph), 78.4 (Zr-OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), 42.0 (Zr-OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>), 36.7, 37.8 (Zr-OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>).

**3. Synthesis of M(OC<sub>6</sub>H<sub>3</sub>Bu<sup>t</sup>CM<sub>2</sub>CH<sub>2</sub>)(OAr')<sub>2</sub> (M = Ti, 3a; M = Zr, 3b).** The monocyclometalated complexes 2 will react with 2,6-di-*tert*-butylphenol (HOAr') in toluene at 120 °C to undergo formation of toluene and excellent yields of the monometalated, bis-aryloxyde 3.

(21) Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, 2, 16.

(22) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, 250, 395. (b) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, 104, 2117.

(23) (a) Dawood, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. J. *J. Chem. Soc., Chem. Commun.* **1982**, 802. (b) Dawood, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1410.

(24) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, 104, 3725.

(25) (a) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row, New York, 1981. (b) Doherty, N. M.; Bercaw, J. K. *J. Am. Chem. Soc.* **1985**, 107, 2670.

Removal of solvent and recrystallization from hexane gives the products as yellow **3a** or white **3b** powdery solids. Alternatively, the bis-benzyl **1** will react with HOAr' (1 equiv) in toluene (120 °C) to give **3** directly. Anal. Calcd for  $TiC_{42}H_{62}O_3$  (**3a**): C, 76.10; H, 9.43. Found: C, 76.36; H, 9.57.  $ZrC_{42}H_{62}O_3$  (**3b**): C, 71.44; H, 8.85. Found: C, 67.88; H, 9.43. **3a**:  $^1H$  NMR (30 °C,  $C_6D_6$ )  $\delta$  1.47 (s,  $OC_6H_3Bu'_2$ ), 1.57 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 1.35 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 3.09 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 7.75 (m, aromatics). **3b**:  $^1H$  NMR (30 °C,  $C_6D_6$ )  $\delta$  1.47 (s,  $OC_6H_3Bu'_2$ ), 1.51 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 1.69 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 2.19 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ). **3a**:  $^{13}C$  NMR (30 °C,  $C_6D_6$ )  $\delta$  111.7 (Ti- $OC_6H_3Bu'CM_e_2CH_2$ ), 47.3 (Ti- $OC_6H_3Bu'CM_e_2CH_2$ ), 37.8 (Ti- $OC_6H_3Bu'CM_e_2CH_2$ ). **3b**:  $^{13}C$  NMR (30 °C,  $C_6D_6$ )  $\delta$  83.1 (Zr- $OC_6H_3Bu'CM_e_2CH_3$ ), 42.8 (Zr- $OC_6H_3Bu'CM_e_2CH_2$ ), 37.2 (Zr- $OC_6H_3Bu'CM_e_2CH_2$ ).

**4.  $M(OC_6H_3Bu'CM_e_2CH_2)(OAr')(CH_2Ph)(py)$  ( $M = Ti, 4a; M = Zr, 4b$ ).** Hexane solutions of monometalated compounds **2** will react with pyridine (excess) to quantitatively give solutions containing **4**. Slow cooling to -15 °C gave the pyridine adducts as yellow **4a** and white **4b** powders. Anal. Calcd for  $TiC_{40}H_{53}O_2N$  (**4a**): C, 77.31; H, 7.85; N, 2.20. Found: C, 77.08; H, 8.29; N, 2.24. **4a**:  $^1H$  NMR (30 °C,  $C_6D_6$ )  $\delta$  1.45 (s,  $OC_6H_3Bu'_2$ ), 1.63 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 1.32 (s), 1.27 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 3.51 (d), 2.49 (d,  $CH_2Ph$ ), 2.30 (d), 1.78 (d,  $OC_6H_3Bu'CM_e_2CH_2$ ), 8.71 (m,  $o-C_5H_5N$ ), 6.5-7.5 (m, other aromatics). **4b**:  $^1H$  NMR (30 °C,  $C_6D_6$ )  $\delta$  1.40 (s,  $OC_6H_3Bu'_2$ ), 1.59 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 1.42 (s), 1.68 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 2.85 (d), 2.31 (d,  $CH_2Ph$ ), 1.85 (d,  $OC_6H_3CM_e_2CH_2$  - other half of AB obscured by Bu' signals), 8.65 (m,  $o-C_5H_5N$ ), 6.4-7.5 (m, other aromatics).

**5.  $Ti(OC_6H_3Bu'CM_e_2CH_2)(OAr')(CH_2SiMe_3)(py)$  (**4c**).** A mixture of  $Ti(CH_2SiMe_3)_4$  (1.35 g) and 2,6-di-*tert*-butylphenol (1.4 g, 2 equiv) in toluene was heated at 120 °C for 12 h in a sealed Pyrex tube. The solvent was removed. The  $^1H$  NMR spectrum of the resulting oil indicated the presence of  $Ti(OC_6H_3Bu'CM_e_2CH_2)(OAr')(CH_2SiMe_3)$  (**2c**).

Addition of pyridine (excess) followed by cooling slowly to -15 °C gave the product as deep orange crystals. **2c**:  $^1H$  NMR (30 °C,  $C_6D_6$ )  $\delta$  1.58 (s,  $OC_6H_3Bu'_2$ ), 1.69 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 1.11 (s), 1.39 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), obscured ( $OC_6H_3Bu'CM_e_2CH_2$ ), 6.9-7.5 (aromatics), 2.54 (d), 2.73 (d,  $CH_2SiMe_3$ ), 0.08 (s,  $CH_2SiMe_3$ ). **4c**:  $^1H$  NMR (30 °C,  $C_6D_6$ )  $\delta$  1.59 (s,  $OC_6H_3Bu'_2$ ), 1.71 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 1.20 (s), 1.41 (s,  $OC_6H_3Bu'CM_e_2CH_2$ ), 1.95 (d), 1.80 (d,  $OC_6H_3Bu'CM_e_2CH_2$ ), 2.79 (d), 1.41 (d,  $CH_2SiMe_3$ ), 0.07 (s,  $CH_2SiMe_3$ ), 8.87 (m,  $o-C_5H_5N$ ), 6.5-7.4 (m, other aromatics).

**6. X-ray Structure Determination of  $Ti(OC_6H_3Bu'CM_e_2CH_2)(OAr')(CH_2SiMe_3)(py)$  (**4c**).** General operating procedures have been outlined previously.<sup>26</sup> A suitable yellow crystal was chosen and transferred to the goniostat with use of standard inert handling techniques and characterized with use of a reciprocal lattice search technique. The structure was solved by a combination of direct methods and Fourier techniques by using the 3372 data with  $F_o > 2.33\delta(F)$ . A final difference Fourier was featureless, the largest peak being 0.45 e/A<sup>3</sup>.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE-821906 to I.P.R.) for support of this research.

**Supplementary Material Available:** Tables of fractional coordinates of hydrogen atoms, anisotropic thermal parameters, complete bond distances and angles, and observed and calculated structure factors for  $Ti(OC_6H_3Bu'CM_e_2CH_2)(OAr')(CH_2SiMe_3)(py)$  (**4c**) (30 pages). Ordering information is given on any current masthead page.

(26) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

## Preparation of Trialkoxymolybdenum(VI) Alkylidyne Complexes, Their Reactions with Acetylenes, and the X-ray Structure of $Mo[C_3(CMe_3)_2][OCH(CF_3)_2]_2(C_5H_5N)_2$ <sup>1</sup>

Laughlin G. McCullough, Richard R. Schrock,\* John C. Dewan, and John C. Murdzek

Contribution from the Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received February 19, 1985

**Abstract:**  $Mo(CMe_3)(CH_2CMe_3)_3$  can be prepared in ~35% yield reproducibly and on a multigram scale by adding  $MoO_2Cl_2$  in tetrahydrofuran to 6 equiv of  $Me_3CCH_2MgCl$  in ether.  $Mo(CMe_3)X_3(dme)$  complexes ( $X = Cl$  or  $Br$ ) can be prepared by adding 3 equiv of  $HX$  to  $Mo(CMe_3)(CH_2CMe_3)_3$  in the presence of 1,2-dimethoxyethane (dme). From  $Mo(CMe_3)Cl_3(dme)$ , a wide variety of alkoxide complexes can be prepared of the type  $Mo(CMe_3)(OR)_3$  ( $OR = OMe, OCHMe_2, OCH_2CMe_3, OMe_2(CF_3), OMe(CF_3)_2$ , and  $O-2,6-C_6H_3(CHMe_2)_2$ ),  $Mo(CMe_3)(OR)_3(dme)$  ( $OR = OCH(CF_3)_2, OMe(CF_3)_2$ , and  $OC(CF_3)_3$ ), or  $Mo(CMe_3)(OR)_2Cl(dme)$  ( $OR = OCH(CF_3)_2, OMe(CF_3)_2$  and  $OC(CF_3)_3$ ). Internal acetylenes do not react with  $Mo(CMe_3)(OCMe_3)_3$ , they are largely polymerized by  $Mo(CMe_3)(OCHMe_2)_3$  and  $Mo(CMe_3)(OCH_2CMe_3)_3$ , and they react in an irreversible, apparently complex, and as yet unelucidated fashion with  $Mo(CMe_3)X_3(dme)$ . Internal acetylenes react smoothly with all fluoroalkoxide complexes (most slowly with  $Mo(CMe_3)[OCMe_2(CF_3)_3]$  and with  $Mo(CMe_3)[O-2,6-C_6H_3(CHMe_2)_2]$  to give new, isolable alkylidyne complexes formed by loss of the *tert*-butyl-substituted acetylene from an intermediate molybdenacyclobutadiene complex. A molybdenacyclobutadiene complex,  $Mo(C_3Et_3)[O-2,6-C_6H_3(CHMe_2)_2]_3$ , can be isolated, although at room temperature in toluene- $d_8$  it is virtually totally dissociated into a mixture of  $Mo(CEt)[O-2,6-C_6H_3(CHMe_2)_2]_3$  and 3-hexyne. Terminal acetylenes react with  $Mo(CMe_3)(OCMe_3)_3$  to produce  $Me_3CC\equiv CH$  and  $Mo(CR)(OCMe_3)_3$ . Reactions between terminal acetylenes and fluoroalkoxide complexes yield deprotonated molybdenacyclobutadiene complexes of the type  $Mo(C_3R_2)(OR')_2$ , some of which can be isolated only as bis ligand adducts,  $Mo(C_3R_2)(OR')_2L_2$  ( $L = py, dme, etc.$ ). Reactions between terminal acetylenes and  $Mo(CMe_3)[O-2,6-C_6H_3(CHMe_2)_2]$  yield mixtures of  $Mo[C_3(CMe_3)R][O-2,6-C_6H_3(CHMe_2)_2]$  and  $2,6-C_6H_3(CHMe_2)_2OH$  from which red crystalline  $Mo[C_3(CMe_3)R][O-2,6-C_6H_3(CHMe_2)_2](py)$  complexes can be isolated upon addition of pyridine ( $R = CMe_3, Pr$ , and  $Ph$ ).  $Mo[C_3(CMe_3)_2][OCH(CF_3)_2](py)_2$  crystallizes in the space group  $C2/c$  with  $a = 18.367$  (3) Å,  $b = 11.025$  (2) Å,  $c = 16.641$  (3) Å,  $\beta = 109.98$  (1)°,  $V = 3166.9$  Å<sup>3</sup>, and  $Z = 4$ . It is a pseudooctahedron with the pyridine ligands trans to a planar  $MoC_3$  ring in which  $Mo-C_\alpha = 1.943$  (3) Å and  $Mo-C_\beta = 2.005$  (4) Å. The two oxygen atoms of the  $OCH(CF_3)_2$  ligands are bent away from the ring system ( $O-Mo-O = 152.2$  (1)°) and the  $\alpha$  *tert*-butyl groups are bent away from the metal ( $Mo-C_\alpha-C = 158.9$  (2)°). The  $OCMe(CF_3)_2, OC(CF_3)_3$ , and  $O-2,6-C_6H_3(CHMe_2)_2$  complexes are excellent catalysts for the metathesis of internal acetylenes. There is evidence for the formation of 4-octyne in the reaction between  $Mo(CPr)(OCMe_3)_3$  and 1-pentyne, presumably via a slow metathesis reaction to give unstable  $Mo(CH)(OCMe_3)_3$ .

The first monomeric alkylidyne complexes, *trans*- $X-(CO)_4M\equiv CR$  ( $M = Mo$  and  $W$ ), were prepared in 1973 by

treating an alkylidene (or carbene) complex of the type  $M-(CO)_5[C(R)(OMe)]$  with  $BX_3$ .<sup>2</sup> In 1978, higher oxidation state