

Multiple Metal–Carbon Bonds. 9.¹ Preparation and Characterization of Several Alkylidene Complexes, $M(\eta^5\text{-C}_5\text{H}_5)_2(\text{alkylidene})\text{X}$ ($M = \text{Ta}$ or Nb), and the X-Ray Structure of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHC}_6\text{H}_5)(\text{CH}_2\text{C}_6\text{H}_5)$. An Investigation of Alkylidene Ligand Rotation

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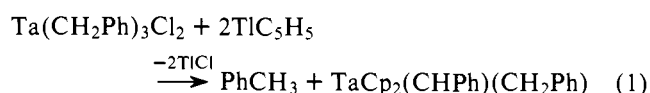
Abstract: The reaction of $\text{Ta}(\text{CH}_2\text{Ph})_3\text{Cl}_2$ or $\text{M}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ with TiC_5H_5 gives $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$ or $\text{MCp}_2(\text{CHCMe}_3)\text{Cl}$ ($M = \text{Nb}$ or Ta), respectively. Cl in $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ can be replaced by CHPh_2 or PMe_3 (to give a cationic complex); $\text{TaCp}_2(\text{CHSiMe}_3)(\text{CH}_3)$ is prepared by deprotonating $[\text{TaCp}_2(\text{CH}_2\text{SiMe}_3)(\text{CH}_3)]^+\text{Br}^-$. All $\text{TaCp}_2(\text{CHR})(\text{X})$ complexes are pseudotetrahedral molecules in which the $=\text{CHR}$ ligand is oriented approximately perpendicular to the C(alkylidene)–Ta–X plane according to ^{13}C and ^1H NMR studies. The $=\text{CHR}$ ligand in all neutral complexes rotates about the C(alkylidene)–Ta bond axis into the C–Ta–X plane with a $\Delta G_{\text{rot}}^\ddagger$ inversely proportional to the size of R. An x-ray structure of $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$ shows that the benzylidene ligand ($\text{Ta}=\text{C}$ 2.07 Å) is in fact not strictly perpendicular to the C(alkylidene)–Ta–X plane in the ground state but is already tipped 5.7° to the inside because of unfavorable steric interaction in what is a rather crowded molecule. These structural results are compared with others.

Introduction

An attempt to make a crowded Nb(V) or Ta(V) alkyl complex often yields an alkylidene complex instead, formally the product of abstraction of one alkyl's α -hydrogen atom by another's α -carbon atom. So far the most stable complexes which have been isolated have two η^5 -cyclopentadienyl rings bound to the metal; this class includes the only known methylene complex, $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$.³ The methylene ligand in $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ does not rotate on the ^1H NMR time scale. Other alkylidene ligands in analogous complexes, however, do. This paper will explore this phenomenon via ^1H NMR and x-ray diffraction studies. Complete preparative details and properties of the $\text{MCp}_2(\text{alkylidene})(\text{X})$ complexes and a cationic relative, $[\text{TaCp}_2(\text{CHCMe}_3)(\text{PMe}_3)]^+\text{Cl}^-$, are also disclosed.

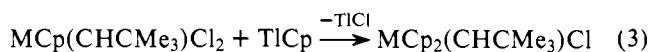
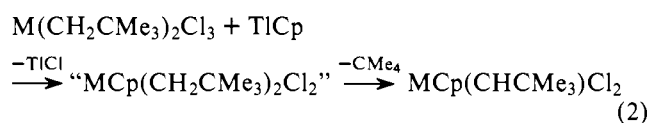
Results

Preparation of Alkylidene Complexes. The reaction between TaMe_3Cl_2 and TiC_5H_5 in toluene is known to yield first TaCpMe_3Cl and then TaCp_2Me_3 , each in high yield, after addition of 1 or 2 mol of TiC_5H_5 , respectively, per Ta.³ In contrast, the corresponding reaction between $\text{Ta}(\text{CH}_2\text{Ph})_3\text{Cl}_2$ and 2 mol of TiC_5H_5 is considerably slower and $\text{TaCp}(\text{CH}_2\text{Ph})_3\text{Cl}$ has not yet been isolated from these reaction mixtures. The only isolated product is $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$. If the reaction is done in benzene, 94% of the theoretical amount of toluene is found in the volatiles. Therefore, the overall stoichiometry is that shown in the equation



$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ does not react with TiC_5H_5 in toluene in 3 days. $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$, however, does. ($\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ is probably too crowded.) Using 1 mol of TiC_5H_5 , $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ can be isolated in high yield.⁴ $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ reacts more slowly with a second mole of TiC_5H_5 to give $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$. A similar reaction

between $\text{Nb}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ and 2 mol of TiC_5H_5 gives $\text{NbCp}_2(\text{CHCMe}_3)\text{Cl}$, possibly via $\text{NbCp}(\text{CHCMe}_3)\text{Cl}_2$.^{4,5} Neopentane has been identified in each case by GLC, though it has not been measured quantitatively; presumably 1 mol is formed. The reaction therefore proceeds as shown in the equations



($M = \text{Nb}$ or Ta). $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{CHCMe}_3)\text{Cl}$ can be prepared analogously employing 2 mol of $\text{TiC}_5\text{H}_4\text{Me}$ in toluene or $\text{LiC}_5\text{H}_4\text{Me}$ in THF.

$\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$, $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\text{CHCMe}_3)\text{Cl}$ ($R = \text{H}$ or Me), and $\text{NbCp}_2(\text{CHCMe}_3)\text{Cl}$ crystallize as brownish-yellow to bronze-colored needles. All are soluble in toluene, acetonitrile, and dichloromethane but only sparingly soluble in saturated hydrocarbons or diethyl ether. $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ does not conduct in acetonitrile. In contrast to $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ ³ these complexes are thermally stable. For example, both $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$ and $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ can be heated in refluxing toluene for several hours and recovered quantitatively unchanged (by ^1H NMR) except for some discoloration. Presumably bimolecular decomposition, the demonstrated mode of decomposition for $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$,^{3a} is sterically blocked when the methylene is substituted with Ph or CMe_3 . They also are not especially air sensitive in the solid state and can be handled briefly in air.

Another member of this class of complexes can be prepared by deprotonating $[\text{TaCp}_2(\text{CH}_2\text{SiMe}_3)(\text{CH}_3)]^+\text{Br}^-$ with $\text{Me}_3\text{P}=\text{CH}_2$ in THF.³ The protons on the carbon between Ta and Si must be considerably more acidic than the methyl protons. The product, $\text{TaCp}_2(\text{CHSiMe}_3)(\text{CH}_3)$, forms ivory plates which are moderately soluble in pentane.

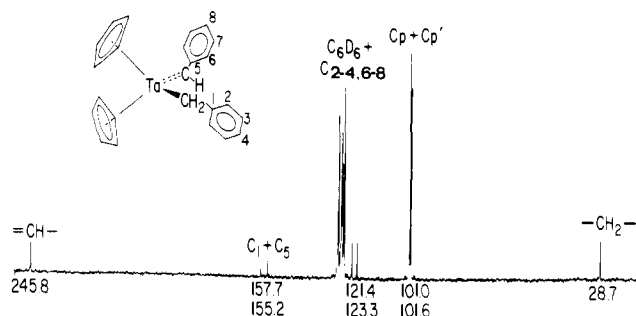
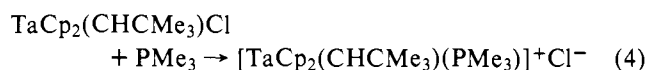


Figure 1. The 22.63-MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$ in C_6D_6 at 30°C .

Two other examples can be prepared by replacing Cl in $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$. Although $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ does not react with LiMe in ether at 25°C in 24 h, it does react readily with $\text{LiCHPh}_2\cdot\text{TMEDA}$ in toluene to give pentane-soluble $\text{TaCp}_2(\text{CHCMe}_3)(\text{CHPh}_2)$. ^{13}C NMR evidence (vide infra) suggests that the diphenylmethyl proton has not transferred to the neopentylidene ligand. The final example is formed simply by mixing $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ with PMe_3 in toluene:



$[\text{TaCp}_2(\text{CHCMe}_3)(\text{PMe}_3)]^+\text{Cl}^-$ separates as a white powder which can be recrystallized from acetonitrile (with ether) as silvery-white platelets. Its equivalent conductance in acetonitrile is in the range expected for a monocationic complex.

$\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ also reacts with carbon monoxide to produce a white, crystalline product which is still being characterized. $[\text{TaCp}_2(\text{CHCMe}_3)(\text{CO})]^+\text{Cl}^-$ is ruled out since we find no neopentylidene-like C_α or H_α by ^{13}C or ^1H NMR, respectively.

NMR Studies. The ^{13}C spectra of the neutral alkylidene complexes all show a characteristic resonance at low field due to the alkylidene α -carbon atom (Table I). In the gated decoupled spectra these peaks are doublets with $^1J_{\text{CH}}$ in the range 105–130 Hz. In the case of $\text{NbCp}_2(\text{CHCMe}_3)\text{Cl}$ the doublet is broadened by coupling to ^{93}Nb ($I = 7/2$, 100%). The cyclopentadienyl ligands are nonequivalent in each case. Therefore, in the ground state the alkylidene ligand plane must be perpendicular to the $\text{C}-\text{Ta}-\text{X}$ plane ($\text{X} = \text{C}$ in an alkyl ligand, Cl, etc; cf. $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)^7$); the molecules have no symmetry. The remaining spectral features are straightforward. An example, the ^{13}C NMR spectrum of $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$, is shown in Figure 1.

The ^1H NMR spectra show the resonance for the alkylidene α proton near τ 0.0 (cf. τ -0.11 in $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$). The factors which influence the ^1H NMR chemical shift of an alkylidene α proton are at present not well known. In $\text{MCp}(\text{CHCMe}_3)\text{Cl}_2^4$ they are found at ca. τ 3 and in $\text{M}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)^9$ at ca. τ 8 ($\text{M} = \text{Nb}$ or Ta). Chemical shifts for α protons in three other carbene-type complexes are as large as or larger than those found here.⁸ At 0°C the nonequivalent cyclopentadienyl ligands usually can be resolved at 100 MHz. In $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$ the molecular asymmetry is manifest in another way; the benzyl α protons are diastereotopic and give rise to an AB quartet with $J_{\text{H}_\text{A}\text{H}_\text{B}} = 10.7$ Hz (see Figure 2).

There is no reason to suspect that the cationic complex, $[\text{TaCp}_2(\text{CHCMe}_3)(\text{PMe}_3)]^+\text{Cl}^-$, is anything other than what it appears to be since all the features noted for the neutral molecules can also be found in its ^1H and ^{13}C NMR spectrum. One might expect some rather different values for (e.g.) τH_α , $^{13}\text{C}_\alpha$, or $^1J_{\text{CH}}$ if the phosphine were interacting significantly with the neopentylidene α -carbon atom. We should note that

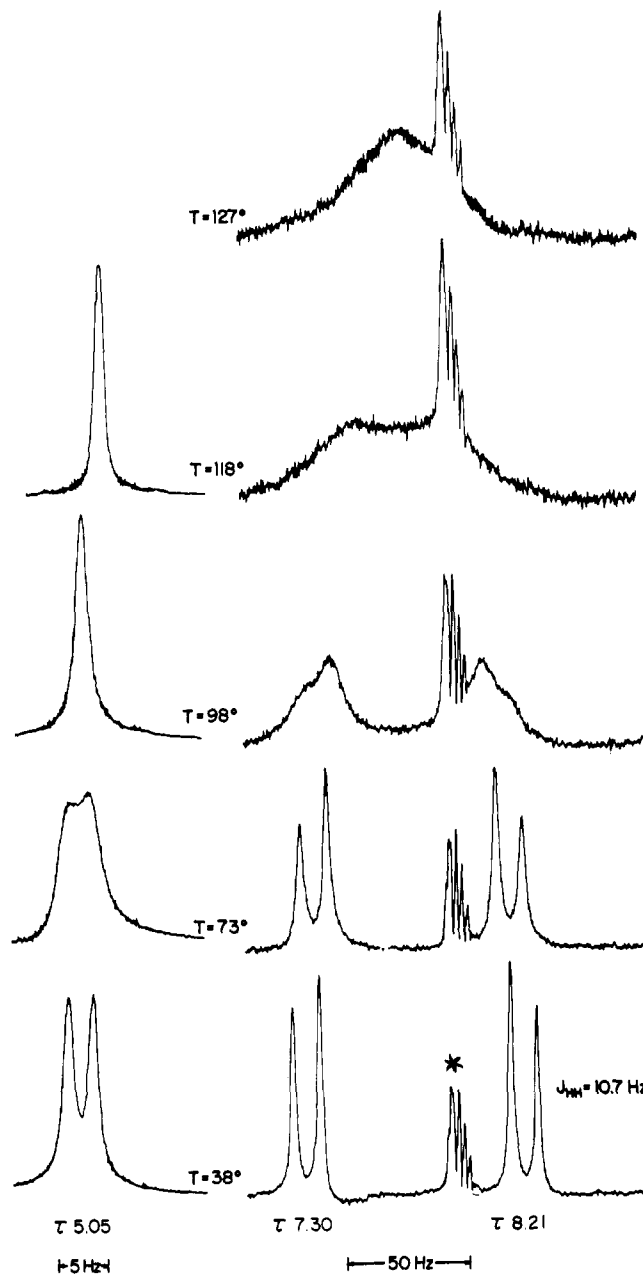
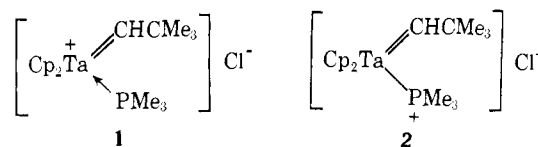


Figure 2. The $\eta^5\text{-C}_5\text{H}_5$ (τ 5.05) and benzyl α -proton signals in the 100-MHz ^1H NMR spectrum of $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$ in toluene- d_8 (* = toluene- d_7 and traces of toluene- d_0).

a formal positive charge does not increase $\delta^{13}\text{C}_\alpha$ significantly (cf. $\text{NbCp}_2(\text{CHCMe}_3)\text{Cl}$). Therefore, the positive charge may be localized primarily on the more electropositive Ta^{5+} (in **1**) or P^{5+} (in **2**), rather than on C_α of the neopentylidene ligand.



As the temperature of a ^1H NMR sample of $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$ in toluene- d_8 is raised, the two cyclopentadienyl proton resonances and the two methylene proton resonances each coalesce to a singlet as shown in Figure 2. During this process the benzylidene α -proton resonance remains sharp. Therefore dynamic processes involving proton transfer to or from the benzylidene ligand must be slow on the

Table I. Some ^{13}C and ^1H NMR Data for Alkylidene Complexes^a

| Compd | $^1\text{H}_\alpha, \tau$ | $\delta^{13}\text{C}_\alpha, \text{ppm}$ | $^1J_{\text{CH}}, \text{Hz}$ | $\Delta G_{\text{rot}}^\ddagger (\pm 0.2), \text{kcal mol}^{-1}$ | T_c, K | $\delta\nu_\infty, \text{Hz}$ |
|--|---------------------------|--|------------------------------|--|-----------------|-------------------------------|
| TaCp ₂ (CHPh)(CH ₂ Ph) | -0.86 ^b | 246 ^c | 127 ^c | 19.2 ^d | 391 | 68 ^d |
| TaCp ₂ (CHCMe ₃)Cl | -0.10 | 274 ^c | 121 ^c | 16.8 ^{b,e} | 323 | 13.0 |
| NbCp ₂ (CHCMe ₃)Cl | -2.12 | 299 ^f | 131 | 15.6 ^b | 294 | 7.2 |
| Ta($\eta^5\text{-C}_5\text{H}_4\text{Me}$) ₂ (CHCMe ₃)Cl | 0.19 | 269 | 119 | 15.9 ^g | 315 | 27 ^g |
| TaCp ₂ (CHCMe ₃)(CHPh ₂) | 0.15 | 267 | 113 | 16.7 | 309 | 5.0 |
| TaCp ₂ (CHSiMe ₃)(CH ₃) | -0.14 | 236 | 107 | 17.1 | 331 | 15.5 |
| [TaCp ₂ (CHCMe ₃)(PMe ₃)] ⁺ Cl ^{-h} | -1.45 ⁱ | 294 ^j | 110 | ≥23 | ≥400 | 28 |

^a Solvent C₆D₆ and $\delta\nu_\infty$ = the chemical shift difference between Cp and Cp' unless otherwise noted. ^b Solvent CD₃C₆D₅. ^c Solvent CD₂Cl₂. ^d Calculated from collapsing benzyl AB quartet; see Experimental Section. ^e $\Delta G^\ddagger = 16.8 \text{ kcal mol}^{-1}$ by complete line shape analysis courtesy of P. Meakin. ^f A broadened doublet [coupling to ^{93}Nb ($I = 9/2, 100\%$)]. ^g Calculated from coalescing methyl groups on $\eta^5\text{-C}_5\text{H}_4\text{Me}$ ligands. ^h Solvent CD₃CN. ⁱ $^3J_{\text{HP}} = 4 \text{ Hz}$. ^j $^2J_{\text{CP}} = 13.8 \text{ Hz}$.

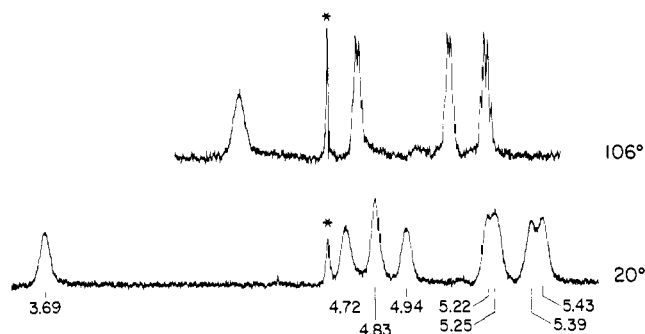


Figure 3. The high- and low-temperature limiting spectra in the cyclopentadienyl region for Ta($\eta^5\text{-C}_5\text{H}_4\text{Me}$)₂(CHCMe₃)Cl in toluene-*d*₈ at 220 MHz (* = an unknown impurity).

^1H NMR time scale (cf. TaCp₂(CD₂)(CH₃)³). A value for ΔG^\ddagger can be obtained from either the cyclopentadienyl or benzyl methylene proton patterns using the Eyring equation and T_c and k_c calculated from the equation¹⁰ $k_c = \pi(\delta\nu_\infty^2 + 6J^2)^{1/2}(2)^{-1/2}$ (see Experimental Section). The two ΔG^\ddagger values so obtained agree within the expected experimental error. Therefore, each spectral change is most likely the result of the same temperature-dependent process in which $\Delta G^\ddagger = 19.2 \pm 0.2 \text{ kcal mol}^{-1}$.

Similar temperature-dependent spectra are observed for the other neutral complexes listed in Table I and ΔG^\ddagger values calculated by similar methods. The cyclopentadienyl groups in [TaCp₂(CHCMe₃)(PMe₃)]⁺Cl⁻, on the other hand, remain nonequivalent up to 90 °C at 90 MHz in CD₃CN ($\Delta G^\ddagger \geq 23 \text{ kcal mol}^{-1}$, ref 11).

Ta($\eta^5\text{-C}_5\text{H}_4\text{Me}$)₂(CHCMe₃)Cl is the most interesting complex to study in detail. The high- and low-temperature limiting spectra in the cyclopentadienyl region at 220 MHz are shown in Figure 3. Since the molecule is asymmetric, the eight cyclopentadienyl protons are nonequivalent, and the cyclopentadienyl methyl groups (not shown in Figure 3) are nonequivalent, at the lower limit. As the temperature is raised the eight protons become four and the two methyl groups (not shown) equilibrate. ΔG^\ddagger , calculated by observing the coalescing methyl groups, is slightly smaller than that found for TaCp₂(CHCMe₃)Cl (Table I). The important point is that one and only one plane of symmetry is created as a result of the averaging process. The validity of this conclusion was checked by analyzing the spectra of Ta($\eta^5\text{-C}_5\text{H}_4\text{Me}$)₂Me₃ and [Ta($\eta^5\text{-C}_5\text{H}_4\text{Me}$)₂Me₂]⁺BF₄⁻ (each has two symmetry planes and therefore two cyclopentadienyl proton multiplet resonances) and Ta($\eta^5\text{-C}_5\text{H}_4\text{Me}$)₂(CH₂)(CH₃) (it has one symmetry plane, and therefore four cyclopentadienyl proton resonances).³

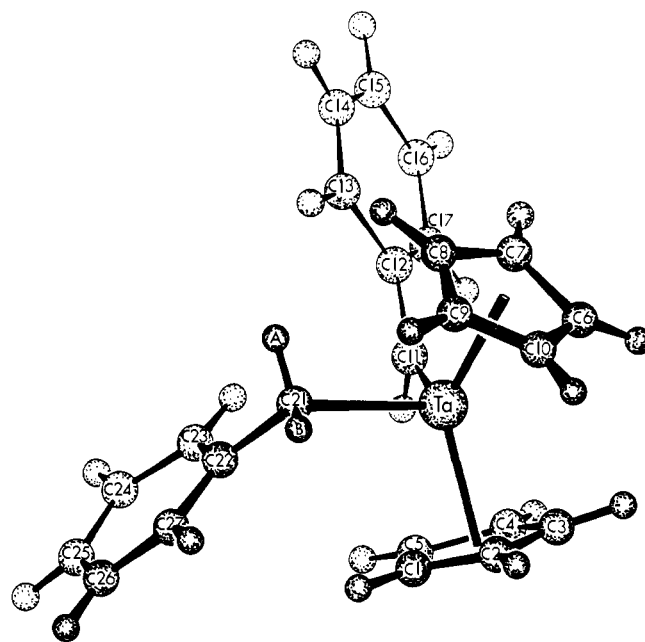


Figure 4. The molecular structure of Ta($\eta^5\text{-C}_5\text{H}_5$)₂(CHC₆H₅)(CH₂C₆H₅).

One of the most intriguing possible explanations of the observed temperature-dependent process is that the alkylidene ligand rotates into the C(alkylidene)-Ta-X plane while the tetrahedral molecular geometry does not change. The most acceptable "proof" that this is the case would be to discover that substituted alkylidene ligands turn away from the most favored orientation (perpendicular to the C(alkylidene)-Ta-X plane) to an extent Φ which varies inversely with the magnitude of ΔG^\ddagger . The molecular structure of TaCp₂(CHPh)(CH₂Ph) was therefore determined by x-ray diffraction and compared (see Discussion) with the structures of TaCp₂(CH₂)(CH₃)⁷ and TaCp₂(CHCMe₃)Cl.¹²

Molecular Structure of Ta($\eta^5\text{-C}_5\text{H}_5$)₂(CHC₆H₅)(CH₂C₆H₅). The unit cell consists of discrete molecules with the structure shown in Figure 4. Details concerning the structural analysis can be found in the Experimental Section. The final positional and thermal parameters are given in Table II. Pertinent interatomic distances and angles are listed in Table III and some of the least-squares planes and dihedral angles in Table IV. All intermolecular distances are larger than 2.50 Å except H(3) - -H(7'), which is 2.35 Å.

The structural features are typical of bis(η^5 -cyclopentadienyl) transition metal complexes. The planar $\eta^5\text{-C}_5\text{H}_5$ groups bend back away from the remaining two ligands creating a

Table II. Final Positional and Thermal Parameters ($\times 10^4$) for Ta(η^5 -C₅H₅)₂(CHC₆H₅)(CH₂C₆H₅)^a

| Atom | x | y | z | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|------------|------------|------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Ta | 1144.3 (6) | -0.3 (4) | 8031.8 (3) | 134.8 (10) | 31.5 (3) | 46.6 (4) | -8.3 (5) | 16.4 (4) | -0.1 (3) |
| C(1) | 3808 (16) | -114 (10) | 7880 (11) | 120 (19) | 64 (10) | 64 (10) | 49 (12) | 18 (11) | -8 (8) |
| C(2) | 3541 (17) | -763 (11) | 8456 (16) | 80 (24) | 65 (11) | 157 (18) | 20 (13) | 46 (17) | 22 (12) |
| C(3) | 3175 (19) | -444 (11) | 9350 (10) | 264 (36) | 59 (9) | 27 (10) | 11 (14) | 14 (15) | 4 (7) |
| C(4) | 3253 (14) | 426 (9) | 9308 (12) | 61 (19) | 33 (7) | 115 (14) | 4 (9) | 16 (13) | 4 (8) |
| C(5) | 3675 (17) | 660 (8) | 8372 (11) | 208 (28) | 39 (6) | 58 (10) | -34 (10) | 25 (14) | 5 (6) |
| C(6) | -295 (17) | -853 (8) | 9003 (9) | 217 (26) | 36 (6) | 45 (9) | -52 (10) | -9 (13) | -1 (6) |
| C(7) | -1354 (17) | -301 (8) | 8444 (11) | 194 (25) | 28 (6) | 64 (11) | -27 (9) | 46 (14) | -2 (6) |
| C(8) | -1452 (16) | -471 (9) | 7422 (11) | 144 (23) | 34 (7) | 72 (11) | -10 (11) | 21 (13) | 3 (7) |
| C(9) | -523 (20) | -1128 (10) | 7287 (13) | 239 (33) | 57 (9) | 89 (15) | -47 (14) | 44 (18) | -26 (9) |
| C(10) | 104 (17) | -1395 (9) | 8212 (14) | 145 (24) | 43 (8) | 139 (17) | -45 (11) | -9 (17) | 14 (10) |
| C(11) | 471 (13) | 1208 (7) | 8309 (9) | 58 (17) | 35 (6) | 57 (9) | 7 (8) | 17 (10) | 16 (6) |
| C(12) | -996 (15) | 1641 (7) | 8236 (9) | 161 (23) | 21 (5) | 40 (8) | -8 (9) | 4 (11) | 12 (5) |
| C(13) | -2270 (16) | 1567 (9) | 7428 (11) | 145 (25) | 48 (8) | 74 (12) | 15 (11) | 7 (14) | 2 (7) |
| C(14) | -3613 (18) | 1956 (11) | 7454 (12) | 140 (27) | 78 (11) | 67 (12) | -7 (14) | -7 (15) | 31 (9) |
| C(15) | -3803 (20) | 2504 (10) | 8208 (15) | 202 (34) | 45 (8) | 107 (17) | 19 (13) | 47 (21) | 33 (10) |
| C(16) | -2621 (22) | 2616 (9) | 8945 (12) | 260 (37) | 39 (8) | 56 (12) | 19 (14) | 44 (17) | 9 (7) |
| C(17) | -1218 (18) | 2209 (8) | 8972 (11) | 204 (30) | 35 (6) | 58 (10) | 6 (11) | 15 (14) | 7 (7) |
| C(21) | 1063 (18) | 204 (9) | 6348 (10) | 193 (27) | 53 (10) | 38 (8) | -24 (11) | 15 (12) | 3 (6) |
| C(22) | 1976 (17) | 846 (11) | 5948 (11) | 136 (25) | 81 (11) | 55 (10) | -5 (13) | 26 (13) | 29 (9) |
| C(23) | 1788 (17) | 1690 (10) | 6150 (11) | 155 (26) | 66 (9) | 69 (12) | 53 (13) | 59 (14) | 33 (8) |
| C(24) | 2582 (17) | 2302 (11) | 5699 (13) | 132 (26) | 83 (11) | 95 (14) | 65 (14) | 51 (17) | 46 (10) |
| C(25) | 3628 (18) | 2073 (11) | 5143 (11) | 158 (28) | 66 (9) | 59 (11) | -8 (13) | -2 (14) | 34 (8) |
| C(26) | 3885 (23) | 1247 (13) | 4955 (13) | 230 (38) | 87 (12) | 91 (15) | -13 (18) | 50 (18) | 1 (11) |
| C(27) | 3014 (20) | 642 (10) | 5332 (10) | 282 (36) | 54 (8) | 31 (9) | -13 (14) | 8 (15) | -8 (7) |

| Atom | x | y | z | Atom | x | y | z |
|-------|-------|-------|------|--------|-------|------|------|
| H(1) | 4074 | -180 | 7196 | H(14) | -4533 | 1829 | 6908 |
| H(2) | 3644 | -1397 | 8307 | H(15) | -4818 | 2803 | 8178 |
| H(3) | 2821 | -781 | 9910 | H(16) | -2779 | 3043 | 9483 |
| H(4) | 3097 | 827 | 9856 | H(17) | -329 | 2327 | 9557 |
| H(5) | 3791 | 1244 | 8103 | H(21A) | -47 | 302 | 6058 |
| H(6) | 91 | -875 | 9746 | H(21B) | 1378 | -355 | 6088 |
| H(7) | -1927 | 152 | 8739 | H(23) | 1086 | 1864 | 6637 |
| H(8) | -2128 | -154 | 6862 | H(24) | 2367 | 2937 | 5785 |
| H(9) | -298 | -1377 | 6624 | H(25) | 4300 | 2522 | 4876 |
| H(10) | 745 | -1929 | 8358 | H(26) | 4640 | 1053 | 4482 |
| H(11) | 1370 | 1590 | 8556 | H(27) | 3159 | 21 | 5177 |
| H(13) | -2158 | 1202 | 6820 | | | | |

^a The estimated standard deviations here and in other tables are given in parentheses. The anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

pseudotetrahedral molecule with an angle between the two Cp centroids (CNT1-Ta-CNT2, Table III) equal to 132.6 (6)^o (132.2^o by dihedral angles; Table IV) and a C(11)-Ta-C(21) angle equal to 95.2 (5)^o. Both are in the range frequently observed for bis(η^5 -cyclopentadienyl) transition metal complexes.^{13,14} The cyclopentadienyl rings are not quite eclipsed; possible factors are the short H(3)-H(7') intermolecular distance and the many short intramolecular interatomic H-H interactions (vide infra).

The most significant Ta-carbon distances are Ta-C(11) and Ta-C(21). The Ta-C(21) bond length of 2.30 (1) Å is characteristic of a single bond (cf., for example, 2.26 (2) Å in Ta(CH₂CMe₃)₃(CCMe₃)-Li(dimethylpiperazine)¹⁵ and 2.246 (12) Å in TaCp₂(CH₂)(CH₃)⁷). The Ta-C(11) bond length of 2.07 (1) Å is believed to be characteristic of a bond order significantly greater than one (cf. 2.026 (10) Å for Ta=CH₂). The difference between Ta-C(21) and Ta-C(11) is 0.23 Å, virtually identical with the difference (0.22 Å) between Ta=CH₂ and Ta-CH₃. These shorter bonds are essentially double bonds if 1.76 Å is believed to be close to a Ta-carbon triple bond length.¹⁵

One prominent structural feature of this molecule is the crowded coordination sphere. Many nonbonding H-H contacts lie in the 2.25-2.60 Å range (Table III). Most of these are between α protons, C(21A), C(21B), or C(11), and phenyl or cyclopentadienyl protons. This is quite likely the reason why

the nonhydrogen atoms on the benzyl and benzylidene ligands (and the cyclopentadienyl ligands) roughly conform to C₂(2) symmetry (although the molecule has no true chemical or crystallographic point symmetry). Short H-H contacts could also explain (1) why the phenyl rings are twisted with respect to the Ta-C α -C β planes (the Ta, C(11), C(12), C₆H₅ and Ta, C(21), C(22), C₆H₅ torsion angles are 41.3 and 60.8^o, respectively; Table IV), and (2) why the benzyl's phenyl ring is *not* turned to the "outside", i.e., between the two cyclopentadienyl ligands (a model shows this is clearly less favorable no matter how the ring is oriented) but to the "inside" toward the benzylidene ligand. The dihedral angle between the Ta, C(21), C(22), and Ta, C(11), C(21) planes is 122^o.

The details of the benzylidene ligand's orientation are particularly important. Unlike the methylene ligand in TaCp₂(CH₂)(CH₃),⁷ the benzylidene ligand (the Ta-C(11)-C(12) plane) is *not* perpendicular to the C(21)-Ta-C(11) plane. The Ta, C(11), C(12); Ta, C(11), C(21) dihedral angle is 95.7^o (Table IV), i.e., it too is turned slightly to the "inside", presumably because of a steric interaction of its phenyl ring with the nearest cyclopentadienyl ligand. But because it is doubly bound to Ta it cannot turn inside as much as the benzyl ligand (the deviation from the perpendicular is only 5.7^o vs. 31.5^o for the benzyl ligand) in the ground state.

Two other features in the molecule may be taken as further evidence of steric crowding; the Ta-C α -C β angles, Ta-

Table III. Interatomic Distances and Angles for $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHC}_6\text{H}_5)(\text{CH}_2\text{C}_6\text{H}_5)^a$

| Interatomic Distances, Å | | | |
|--|------------|-------------------------------|------------|
| Ta-C(11) | 2.07 (1) | C ₆ H ₅ | |
| Ta-C(21) | 2.30 (1) | C(12)-C(13) | 1.43 (2) |
| | | C(13)-C(14) | 1.35 (2) |
| C(11)-C(12) | 1.46 (2) | C(14)-C(15) | 1.38 (3) |
| C(21)-C(22) | 1.47 (2) | C(15)-C(16) | 1.33 (2) |
| | | C(16)-C(17) | 1.39 (2) |
| Ta-C(1) | 2.41 (1) | C(17)-C(12) | 1.39 (2) |
| Ta-C(2) | 2.42 (2) | C(22)-C(23) | 1.39 (2) |
| Ta-C(3) | 2.41 (1) | C(23)-C(24) | 1.41 (2) |
| Ta-C(4) | 2.41 (1) | C(24)-C(25) | 1.35 (2) |
| Ta-C(5) | 2.44 (1) | C(25)-C(26) | 1.37 (3) |
| Ta-C(6) | 2.41 (1) | C(26)-C(27) | 1.39 (3) |
| Ta-C(7) | 2.42 (2) | C(27)-C(22) | 1.39 (2) |
| Ta-C(8) | 2.42 (1) | | 1.38 (1) |
| Ta-C(9) | 2.43 (2) | | |
| Ta-C(10) | 2.44 (1) | C ₅ H ₅ | |
| | 2.42 (1) | C(1)-C(2) | 1.34 (3) |
| | | C(2)-C(3) | 1.41 (3) |
| Nonbonding | | C(3)-C(4) | 1.39 (2) |
| H(11)-...H(4) | 2.45 | C(4)-C(5) | 1.44 (2) |
| H(11)-...H(5) | 2.39 | C(5)-C(1) | 1.42 (2) |
| H(11)-...H(23) | 2.62 | C(6)-C(7) | 1.41 (2) |
| H(11)-...H(17) | 2.50 | C(7)-C(8) | 1.41 (2) |
| H(21A)-...H(8) | 2.41 | C(8)-C(9) | 1.36 (2) |
| H(21B)-...H(9) | 2.40 | C(9)-C(10) | 1.35 (2) |
| H(21B)-...H(1) | 2.60 | C(10)-C(6) | 1.47 (2) |
| H(21B)-...H(27) | 2.25 | | 1.40 (1) |
| H(10)-...H(2) | 2.71 | | |
| H(6)-...H(3) | 2.39 | | |
| Interatomic Angles, deg | | | |
| C(11)-Ta-C(21) | 95.2 (5) | Ta-C(11)-C(12) | 135.2 (7) |
| CNT1-Ta-CNT2 | 132.6 (6) | Ta-C(21)-C(22) | 123.1 (10) |
| CNT1-Ta-C(11) | 104.5 (5) | | |
| CNT1-Ta-C(21) | 105.8 (5) | C(11)-C(12)-C(13) | 125.6 (11) |
| CNT2-Ta-C(11) | 109.3 (5) | C(11)-C(12)-C(17) | 119.8 (11) |
| CNT2-Ta-C(21) | 103.2 (5) | | |
| | | C(21)-C(22)-C(23) | 120.6 (14) |
| | | C(21)-C(22)-C(27) | 121.9 (14) |
| Average angles | | | |
| C-Ta-C(C ₅ H ₅) | 33.6 (3) | | |
| C-C-C(C ₅ H ₅) | 108.0 (10) | | |
| C-C-C(C ₆ H ₅) | 119.9 (7) | | |

^a The estimated error of the mean was calculated according to $[\sum_i (d_i - \bar{d})^2 / n(n-1)]^{1/2}$ where d_i and \bar{d} are the distance or angle and mean value, respectively.

C(11)-C(12) (135.2 (7)°) and Ta-C(21)-C(22) (123.1 (10)°), are larger than expected. If we can assume that crowding affects the benzyl and benzylidene ligands about equally, then the difference between these two values (12°) is about what one might expect to be the difference between sp³- and sp²-hybridized α -carbon atoms. The larger Ta-C(11)-C(12) angle also seems to mitigate the possibly more severe steric problems caused by a shorter Ta-C(11) bond.

Discussion

We will not be concerned here with various aspects of the preparation of the complexes since the details of the crucial α -hydrogen abstraction step are still not fully understood (see ref 1 for a discussion). Neither do we yet know why $\delta^{13}\text{C}_\alpha$, $^1J_{\text{CH}}$, or τH_α vary from one type of complex to another as much as they do. What we wish to concentrate on is the phenomenon of alkylidene rotation into the C(alkylidene)-Ta-X plane.

The phenomenon probably can now be called a true alkylidene rotation. Various alternatives such as inversion at the metal center, loss of Cl⁻ or PR₃, or H scrambling processes which involve the alkylidene ligand can all be ruled out. The process is not intermolecular based on steric considerations and due to the fact that $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$ decomposes inter-

molecularly.³ Invoking $\eta^5\text{-C}_5\text{H}_5 \rightarrow \eta^1\text{-C}_5\text{H}_5$ alone also accomplishes nothing; the alkylidene must still rotate.

The structural data for $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$,⁷ $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$, and $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ ¹² show them to be very similar, pseudotetrahedral complexes with planar $\eta^5\text{-C}_5\text{H}_5$ rings, a Cp-Ta-Cp angle of about 135°, and a C(alkylidene)-Ta-X angle of 95–100°. All single bond lengths (Ta-Cl, C-H, etc.) are normal. The Ta-C(alkyl) bond lengths (alkyl = methyl and benzyl) are around 2.25 Å, reasonable for a single bond between Ta and C(alkyl). The Ta-C(alkylidene) bond lengths, however, are shorter by ca. 0.25 Å compared to the corresponding single bond lengths. Clearly these bonds have a significant amount of double bond character.

One of the two most interesting differences between the three structures is the variation in Φ (Table V). The alkylidene is already rotated partially in the *ground-state configuration* (in the solid state) to an extent roughly proportional to the size of R (R = H < C₆H₅ < CMe₃) presumably owing to increasingly severe steric problems associated with a perpendicular orientation ($\Phi = 0^\circ$). The energy needed to further rotate the alkylidene in the same direction into the C(alkylidene)-Ta-X plane therefore decreases in the same order. One conclusion we can draw from the fact that $\Delta G_{\text{rot}}^\ddagger$ decreases markedly for

Table IV. Least-Square Planes and Dihedral Angles for $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHC}_6\text{H}_5)(\text{CH}_2\text{C}_6\text{H}_5)^a$

| | |
|---|-----------------------|
| 1. $0.9089X - 0.0354Y + 0.4156Z - 5.736 = 0$ C(1) -0.01, C(2) 0.01, C(3) 0.00, C(4) 0.00, C(5) 0.01 Ta* -2.10 | |
| 2. $0.7834X + 0.6201Y - 0.0429Z + 3.297 = 0$ C(6) 0.03, C(7) -0.02, C(8) 0.00, C(9) 0.02, C(10) -0.03 Ta* 2.11 | |
| 3. $0.4196X + 0.7587Y - 0.4983Z + 4.688 = 0$ C(12) -0.03, C(13) 0.03, C(14) -0.02, C(15) 0.00, C(16) 0.00, C(17) 0.01 | |
| 4. $0.5870X - 0.0478Y + 0.8082Z - 6.561 = 0$ C(22) 0.00, C(23) 0.03, C(24) -0.03, C(25) 0.01, C(26) 0.02, C(27) -0.03 | |
| | Dihedral Angles |
| C(1)-C(5) 132.2 | Ta, C(11), C(12) 41.3 |
| C(6)-C(10) | C(12)-C(17) |
| C(12)-C(17) 101.1 | Ta, C(21), C(22) 60.8 |
| C(22)-C(27) | C(22)-C(27) |
| Ta, C(21), C(22) 121.5 | Ta, C(11), C(12) 95.7 |
| Ta, C(11), C(21) | Ta, C(11), C(21) |

^a The equations are based on the Cartesian coordinate system (*a*, *b*, *c**). The tantalum atoms in planes 1 and 2 were not included in the refinement.

a relatively small Φ (10° for $\text{R} = \text{CMe}_3$) is that *the overlap of the orbitals forming the π bond must be relatively poor.*

The data for other complexes listed in Table I are at least consistent with the concept of a "sterically assisted" rotation of the alkylidene ligand. For example, the difference in $\Delta G_{\text{rot}}^\ddagger$ for $\text{R} = \text{SiMe}_3$ vs. CMe_3 , though barely significant, is in the right direction because Si is larger than C and the SiMe_3 group therefore *less* demanding sterically. The slightly lower $\Delta G_{\text{rot}}^\ddagger$ on changing $\eta^5\text{-C}_5\text{H}_5$ to $\eta^5\text{-C}_5\text{H}_4\text{Me}$ is again in the right direction. The lower $\Delta G_{\text{rot}}^\ddagger$ on changing from Ta to Nb is characteristic of fluxional processes in general.¹⁷ The effect of changing X from Cl to CH_3 or a larger, but not spherical ligand, CHPh_2 , cannot be assessed accurately, but it is probably not great. Exchanging Cl for the relatively large PMe_3 ligand should actually encourage the neopentylidene ligand to turn outside (if steric interaction between H_α and CH_3 is comparatively unimportant) yet $\Delta G_{\text{rot}}^\ddagger$ increases dramatically. This may be due largely to the effect of an overall positive charge, most likely shared between Ta and P (see below).

In the transition state, in which CHR is rotated into the C-Ta-X plane ($|\Phi| = 90^\circ$), the $2p_z$ orbital on C_α is now orthogonal to the metal orbital it overlapped with to form the π bond in the ground state.^{3,13,14,16,18} But there probably is no relatively low energy metal orbital of the appropriate symmetry to form a π bond if $|\Phi| = 90^\circ$ in this particular type of complex.¹⁶ (*In general* this is probably not true and barriers to rotation may be more commonly small.) If we can assume that the $\text{M}=\text{CHR}$ bond is polarized the same way as the $\text{Ta}=\text{CH}_2$ bond ($+\text{M}=\bar{\text{C}}$), and that the polarization will be the same in the transition state, then the transition state can be described in valence bond terms as $+\text{M}-\bar{\text{C}}\text{HR}$. If the complex carries a

positive charge overall then this transition state would be more difficult to attain for electronic reasons as the large estimated $\Delta G_{\text{rot}}^\ddagger$ for $[\text{TaCp}_2(\text{CHCMe}_3)(\text{PMe}_3)]^+\text{Cl}^-$ (Table I) suggests.

The second major difference between the three structures is the variation in θ_{ene} (Table V). For a given R, θ_{ene} , like θ_{yl} [e.g., 94° in $\text{Hf}(\text{CH}_2\text{Ph})_4$ ¹⁹ to 123° in $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$], may vary considerably depending on the congestion about the metal or (in special cases like CH_2Ph) on other factors such as valence-electron count.²⁰ But within the 18-valence-electron sterically congested $\text{TaCp}_2(\text{alkylidene})\text{X}$ family θ_{ene} most likely depends primarily on the size of R. When $\text{R} = \text{H}$ θ_{ene} is probably relatively insensitive to steric factors, and, within the accuracy of the x-ray method, probably constitutes a lower limit.

Experimental Section

$\text{Ta}(\text{CH}_2\text{Ph})_3\text{Cl}_2$,²¹ $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$,⁴ and $[\text{TaCp}_2(\text{CH}_2\text{SiMe}_3)(\text{Me})]^+\text{Br}^-$ (ref 3) were prepared by published methods. TiC_5H_5 (Strem) was sublimed before use. $\text{LiCHPh}_2\cdot\text{TMEDA}$ was prepared from $\text{Li}(\text{butyl})\cdot\text{TMEDA}$ and diphenylmethane. Decolorizing charcoal (Darco) was heated in vacuo overnight at 150°C before use. Elemental analyses were done by Alfred P. Bernhardt. ^1H NMR spectra were run at 90 MHz (Perkin-Elmer) and ^{13}C spectra at 22.63 or 67.89 MHz (Bruker).

(1) **Preparation of $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$.** A mixture of 2.62 g of $\text{Ta}(\text{CH}_2\text{Ph})_3\text{Cl}_2$ and 2.69 g of TiC_5H_5 was stirred for 1 week in 20 mL of toluene. TiCl_4 was filtered off and nearly all of the toluene removed in vacuo. Pentane was added until the solution just became cloudy. Some decolorizing charcoal was added and the mixture was filtered. The filtrate was cooled to -30°C for 8 h to give 1.29 g (52%) of product as light brown-orange needles. The volatiles from a 5-day reaction between 1.05 g of $\text{Ta}(\text{CH}_2\text{Ph})_3\text{Cl}_2$ and 1.08 g of TiC_5H_5 in C_6H_6 contained 94% of the expected toluene by quantitative GLC comparison with a standard.

Anal. Calcd for $\text{TaC}_24\text{H}_{23}$: C, 58.55; H, 4.70. Found: C, 58.18; H, 4.76. ^1H NMR (toluene-*d*₈, 100 MHz): τ -0.86 (s, 1, benzylidene H_α), 2.6-3.1 (m, 10, phenyl), 5.04 (s, 5, Cp), 5.06 (s, 5, Cp'), 7.30 (d, 1, $J = 10.7$ Hz, benzyl H_α), 8.21 (d, 1, $J = 10.7$ Hz, benzyl H_α). ^{13}C (from Me_4Si , ^1H decoupled, C_6D_6): 246 (benzylidene C_α), 157.7 and 155.2 (C_β on benzyl and benzylidene), 123.3 and 121.4 (C_γ on benzyl and benzylidene), ca. 130 (m, other phenyl carbon atoms), 101.6 (Cp), 101.0 (Cp'), 28.7 (benzyl C_α); (gated decoupled, CD_2Cl_2) 246 (d, $^1J_{\text{CH}} = 127$, benzylidene C_α), 102 (complex d, $^1J_{\text{CH}} = 177$, Cp and Cp'), 28.2 ppm (t, $^1J_{\text{CH}} = 123$, benzyl C_α); the phenyl region is complex (see Figure 1).

(2) **Preparation of $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$.** $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ (3.0 g) and 3.8 g of TiC_5H_5 were stirred in toluene for 24 h. TiCl_4 (3.9 g) was filtered off and most of the toluene removed from the filtrate in vacuo. Addition of pentane gave off-yellow, fluffy crystals. This product was stirred in acetonitrile and any insoluble TiC_5H_5 filtered off. The volume of the filtrate was decreased by removing solvent in vacuo until crystals began to form. After this solution had stood at -40°C overnight 1.2 g of gold-orange needles (41%) was filtered off.

Anal. Calcd for $\text{TaC}_{15}\text{H}_{20}\text{Cl}$: C, 43.23; H, 4.85; Cl, 8.51. Found: C, 43.13; H, 4.93; Cl, 8.60. ^1H NMR (C_6D_6): τ -0.10 (1, s, $=\text{CH}-$), 4.55 (s, s, Cp), 4.69 (s, s, Cp'), 8.70 (9, s, CMe_3); the τ 4.55 and 4.69 singlets are broad at 60 MHz and are beginning to merge at 35°C . ^{13}C NMR (from Me_4Si , gated decoupled, CD_2Cl_2): 274 (d, $^1J_{\text{CH}} = 121$ Hz, neopentylidene C_α), 104.4 and 103.2 (d, $^1J_{\text{CH}} = 177$ Hz, Cp

Table V. A Comparison of Φ , θ_{ene} , and θ_{yl} in Three Complexes^a

| | Φ , deg | $\Delta G_{\text{rot}}^\ddagger$ (± 0.2), kcal mol ⁻¹ | θ_{ene} , deg | θ_{yl} , deg |
|--|-----------------------|---|-----------------------------|----------------------------|
| $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)^7$ | 0 (3) | \geq ca. 21 ^b | 126 (5) | |
| $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$ | -5.7 (5) ^c | 19.2 | 135.2 (7) | 123.1 (10) |
| $\text{TaCp}_2(\text{CHCMe}_3)(\text{Cl})^{7,12}$ | 10.3 (5) ^c | 16.8 | 150.4 (5) | [128 (4)] ^d 15 |

^a Φ is the deviation of the alkylidene plane from an orientation 90° to the C-Ta-X plane (X = Cl, CH_3 , etc., a negative value implies rotation to the "inside"). θ_{ene} is the Ta-C(alkylidene)-R angle and θ_{yl} the Ta-C(alkyl)-R angle. ^b Lauher and Hoffmann¹⁶ estimated $\Delta G^\ddagger = 27$ kcal mol⁻¹ in $[\text{TiCp}_2(\text{CH}_2)(\text{CH}_3)]^-$. ^c Whether the alkylidene rotates to the inside or to the outside is probably very sensitive to intra- and possibly also intermolecular interactions. This subject will be discussed more fully elsewhere. ^d This value is the Ta- CH_2 - CMe_3 angle found for a neopentyl group in $[(\text{Me}_3\text{CCH}_2)_3\text{Ta}=\text{CCMe}_3]\cdot\text{Li}(\text{dmp})$.

and Cp'), 49.3 (s, neopentylidene C_β), 33.3 ppm (q, $^1J_{\text{CH}} = 125$ Hz, neopentylidene C_γ).

The resistance of a solution of 100 mg of $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ in 50 mL of CH_3CN was 74 000 Ω ; therefore $\Lambda \approx 3$ ($\Lambda \approx 100$ if fully ionized; cf. $[\text{TaCp}_2(\text{CHCMe}_3)(\text{PMe}_3)]^+\text{Cl}^-$).

(3) Preparation of $\text{Nb}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$. A solution of 2.08 g of $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$ in 20 mL of pentane was slowly added over 0.5 h to a briskly stirred suspension of 5.40 g of NbCl_5 in 30 mL of pentane. After 10 min the mixture was filtered and the pentane removed in vacuo to give red-orange crystals which melted near room temperature, yield 2.0–2.7 g (60–80% vs. Zn). $\text{Nb}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ crystallizes at 0 °C and is stable at –30 °C for several hours but after ca. 15 min at 25 °C decomposes suddenly evolving volumes of dense brown smoke. $\text{Nb}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ also decomposes in pentane, ether, and toluene, rapidly near 25 °C, and slowly at –20 °C to give a brown, insoluble precipitate. We do not know why it is comparatively stable at 25 °C in pentane in the presence of NbCl_5 . $^1\text{H NMR}$ (C_6D_6): τ 6.23 (br s, 2), 8.80 (s, 9).

(4) Preparation of $\text{NbCp}_2(\text{CHCMe}_3)\text{Cl}$. Thallium cyclopentadienide (3.31 g) was added to 2.10 g of $\text{Nb}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ in 40 mL of toluene and the mixture stirred for 6 h. TiCl_4 was filtered off and the solvent removed in vacuo. Pentane was added to the residue and 1.15 g of product isolated by filtration (57% crude yield). Recrystallization from acetonitrile gave 0.85 g (42%) of golden orange needles of pure $\text{NbCp}_2(\text{CHCMe}_3)\text{Cl}$.

$^1\text{H NMR}$ (C_6D_6): τ –2.12 (s, 1), 4.48 (br s, 10, Cp and Cp' at 35 °C, 60 MHz), 8.74 (s, 9). $^{13}\text{C NMR}$ (from Me_4Si , C_6D_6 , gated): 299 (d, $^1J_{\text{CH}} = 131$ Hz, alkylidene C_α), 106.3 (d, $^1J_{\text{CH}} = 177$ Hz, Cp), 104.3 (d, $^1J_{\text{CH}} = 177$ Hz, Cp'), 51.4 (s, alkylidene C_β), 31.8 ppm (q, $^1J_{\text{CH}} = 125$ Hz, alkylidene C_γ).

(5) Preparation of $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{CHCMe}_3)\text{Cl}$. (a) Using $\text{TiCl}_3\text{H}_4\text{Me}$. A solution of $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ was prepared by adding 4.55 g of $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$ in 25 mL of toluene to a vigorously stirred suspension of 7.91 g of TaCl_5 in 75 mL of toluene over 1 h. After ZnCl_2 was filtered off 12.5 g of $\text{TiCl}_3\text{H}_4\text{Me}$ was added and the mixture stirred overnight. The brown mixture was filtered, the solvent removed in vacuo, and the residue extracted with 50 mL of hexane. Darco (1 g) was added and the mixture was filtered. The filtrate's volume was reduced in vacuo to 25 mL and the solution stood at –30 °C to give 3.0 g of buff-colored product. Reducing the volume further to 10 mL and standing at –30 °C gave an additional 0.8 g, total crude yield 3.8 g (39%). Pure needles can be obtained by recrystallization from acetonitrile at –30 °C.

(b) Using $\text{LiC}_5\text{H}_4\text{Me}$. $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ (5.55 g, 12.9 mmol) was dissolved in THF (50 mL) in a 250-mL round-bottom flask containing a magnetic stir bar. A dropping funnel containing $\text{LiC}_5\text{H}_4\text{Me}$ (2.49 g, 28.9 mmol) in THF (60 mL) was attached. After the flask was cooled to –78 °C the $\text{LiC}_5\text{H}_4\text{Me}$ solution was added dropwise to the stirred solution over 90 min. The mixture was stirred while warming to room temperature and the solvent was removed in vacuo. The product was extracted into hexane and filtered (weight of off-white solid 1.15 g; theory for LiCl and unreacted $\text{LiC}_5\text{H}_4\text{Me}$ is 1.36 g). The hexane was removed in vacuo and the crude product dissolved in a minimum volume of CH_3CN . The solution was filtered and stood at –40 °C for 18 h. Crystalline $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{CHCMe}_3)\text{Cl}$ (3.47 g, 60% yield) was filtered and dried in vacuo.

$^1\text{H NMR}$ (toluene- d_8 , 20 °C, 220 MHz; see Figure 3): τ 0.19 (s, 1, =CH–), 3.69, 4.72, 4.83, 4.94, 5.22, 5.25, 5.39, and 5.43 (m, 1 each, 8 cyclopentadienyl protons), 8.03 (s, 3, methyl), 8.33 (s, 3, methyl'), 8.86 (s, 9, CMe_3); at 106 °C 0.14 (s, 1, =CH–), 4.34, 4.76, 5.09, 5.22 (m, 2 each, 8 cyclopentadienyl protons), 8.11 (s, 6, methyl), 8.86 (s, 9, CMe_3). $^{13}\text{C NMR}$ (from Me_4Si , C_6D_6 , gated, 67.89 MHz): 269.4 (d, $J = 119$ Hz, alkylidene C_α), 122.7 (s, ring C-Me), 118.2 (s, ring C-Me), ca. 110–100 (complex m, 6 ring carbons), 99.1 (d, $J = 171$ Hz, ring carbon), 94.9 (d, $J = 177$ Hz, ring carbon), 48.7 (s, alkylidene C_β), 33.9 (q, $J = 124$ Hz, alkylidene C_γ), 16.0 (q, $J = 124$ Hz, ring CH_3), 15.1 ppm (q, $J = 128$ Hz, ring CH_3).

(6) Preparation of $\text{TaCp}_2(\text{CHCMe}_3)(\text{CHPh}_2)$. $\text{LiCHPh}_2\text{-TMEDA}$ (1.05 g, 3.62 mmol) was added to a stirred solution of $\text{Cp}_2\text{Ta}(\text{CHCMe}_3)\text{Cl}$ (1.50 g, 3.60 mmol) in 30 mL of toluene. The mixture was stirred for 1.5 h and filtered (0.18 g of white solid; theory for LiCl 0.15 g), and the solvent was removed in vacuo. The dark oil was extracted into approximately 50 mL of hexane. Addition of ether (10 mL) precipitated 0.82 g of a cream-colored solid. The mother liquor was reduced in vacuo to an oil. Addition of a minimal volume of hexane followed by ether precipitated an additional 0.21 g of product, total

yield 52%. The product can be recrystallized from hexane/ether mixtures.

$^1\text{H NMR}$ (C_6D_6): τ 0.15 (s, 1, =CH–), 2.70–3.15 (m, 10, Ph), 4.96 (s, 5, Cp), 5.00 (s, 5, Cp'), 5.65 (s, 1, – CHPh_2), 8.65 (s, 9, CMe_3). $^{13}\text{C NMR}$ (from Me_4Si , C_6D_6 , gated, 67.89 MHz): 267.4 (d, $J = 113$ Hz, alkylidene C_α), phenyl region complex and indicative of two non-equivalent phenyl groups, 102.9 (d, $J = 176$ Hz, Cp), 99.7 (d, $J = 176$ Hz, Cp'), 50.3 (s, alkylidene C_β), 48.3 (d, $J = 122$ Hz, CHPh_2), 34.3 ppm (q, $J = 123$ Hz, alkylidene C_γ).

(7) Preparation of $\text{TaCp}_2(\text{CHSiMe}_3)(\text{CH}_3)$. A suspension of 3.0 g of $[\text{TaCp}_2(\text{CH}_2\text{SiMe}_3)(\text{CH}_3)]^+\text{Br}^-$ in 25 mL of THF was treated with 1.60 g of $\text{Me}_3\text{P}=\text{CH}_2$ in 10 mL of THF. After stirring for 10 min all solvent was removed in vacuo and the residue was extracted with 125 mL of pentane. Decolorizing charcoal was added and the mixture was filtered. White crystals were filtered off as the pentane was removed in vacuo, total yield 1.30 g (52%).

Anal. Calcd for $\text{TaC}_{15}\text{H}_{23}\text{Si}$: C, 43.69; H, 5.62. Found: C, 43.71; H, 5.68. $^1\text{H NMR}$ (C_6D_6 , 220 MHz): τ –0.14 (s, 1, =CH–), 4.74 (s, 5, Cp), 4.91 (s, 5, Cp'), 9.66 (s, 9, SiMe_3), 9.82 (s, 3, TaMe). $^{13}\text{C NMR}$ (from Me_4Si , gated decoupled, C_6D_6): 236 (d, $^1J_{\text{CH}} = 107$ Hz, alkylidene C_α), 102.8 (d, $^1J_{\text{CH}} = 177$ Hz, Cp), 101.3 (d, $^1J_{\text{CH}} = 177$ Hz, Cp'), 3.8 (q, $^1J_{\text{CH}} = 118$ Hz, TaMe or SiMe_3), –0.5 ppm (q, $^1J_{\text{CH}} = 124$ Hz, SiMe_3 or TaMe).

(8) Preparation of $[\text{TaCp}_2(\text{CHCMe}_3)(\text{PMe}_3)]^+\text{Cl}^-$. PMe_3 (1.0 mL) was added to a solution of 2.0 g of $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ in 10 mL of toluene. After stirring overnight 2.3 g of white powder was filtered off (97%). This was recrystallized from acetonitrile to give silvery-white plates.

Anal. Calcd for $\text{TaC}_{18}\text{H}_{29}\text{ClP}$: C, 43.86; H, 5.94. Found: C, 43.91; H, 5.90. $^1\text{H NMR}$ (CD_3CN , 220 MHz): τ –1.45 (d, $^3J_{\text{HP}} = 4$ Hz, =CH–), 4.09 (d, $^3J_{\text{HP}} = 2.2$ Hz, Cp), 4.12 (d, $^3J_{\text{HP}} = 2.2$ Hz, Cp'), 8.34 (d, $^2J_{\text{HP}} = 10$ Hz, PMe_3), 8.95 (s, CMe_3). $^{13}\text{C NMR}$ (from Me_4Si , ^1H decoupled, CD_3CN): 294 (d, $^2J_{\text{CP}} = 13.8$ Hz, neopentylidene C_α), 102.1 (poor d, $^2J_{\text{CP}} \leq 1$ Hz, Cp), 98.8 (poor d, $^2J_{\text{CP}} \leq 1$ Hz, Cp'), 53.6 (poor d, $^3J_{\text{CP}} \approx 1$ Hz, neopentylidene C_β), 32.8 (d, $^4J_{\text{CP}} = 3.0$ Hz, neopentylidene C_γ), 22.1 ppm (d, $^1J_{\text{CP}} = 33.5$ Hz, PMe_3). In the gated decoupled spectrum the $^1J_{\text{CH}}$ values (Hz) were 110 (neopentylidene C_α), 180 (Cp), 180 (Cp'), 122 (neopentylidene C_γ), and 130 (PMe_3).

The resistance of a solution of 100 mg of the product in 50 mL of acetonitrile was 2600 Ω ; therefore $\Lambda = 94$.

Calculations of ΔG^\ddagger . For $\text{TaCp}_2(\text{CHPh})(\text{CH}_2\text{Ph})$ at 100 MHz the chemical shift difference between Cp and Cp' was plotted vs. T up to the point where the two began to broaden, and extrapolated to T_c (349 K) to give $\delta\nu_\infty = 2.6$ Hz at T_c (in this case $\delta\nu_\infty$ was directly proportional to T). Therefore $k_c = 5.8$ s $^{-1}$ and $\Delta G^\ddagger = 19.2$ kcal mol $^{-1}$. ΔG^\ddagger varies little with $\Delta\nu_\infty$ (<0.1 kcal mol $^{-1}$ at 349 K for $\delta\nu_\infty = 2.3$ –2.8 Hz) but does with T_c (from 18.9 at 340 K to 20.1 at 360 K).

Calculating ΔG^\ddagger from the benzyl α -proton AB pattern is more accurate. $\delta\nu_\infty$ varies inversely with T . At $T_c = 391$ K, $\delta\nu_\infty = 68$ Hz and $J_{\text{H}_A\text{H}_B} = 10.7$ Hz. Therefore $k_c = 162$ s $^{-1}$ and $\Delta G^\ddagger_{391} = 19.2$ kcal mol $^{-1}$. A reasonable error in ΔG^\ddagger is ± 0.2 kcal mol $^{-1}$.

Other calculations of ΔG^\ddagger were done as above by observing coalescing cyclopentadienyl singlets with the exception of $\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{CHCMe}_3)\text{Cl}$ where the coalescing methyl singlet resonances were followed.

Crystal Structure. Cell and Intensity Data. Crystals of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHC}_6\text{H}_5)(\text{CH}_2\text{C}_6\text{H}_5)$ from toluene are monoclinic with $a = 8.836$ (2), $b = 15.955$ (5), $c = 13.617$ (9) Å, and $\beta = 100.20$ (4)°. The space group is $P2_1/c$ ($h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$ extinctions). The calculated density for four molecules per cell is 1.73 g/cm 3 .

Crystals were sealed in capillaries in a nitrogen-filled drybox. A prismatic crystal $0.17 \times 0.32 \times 0.50$ mm was used for data collection on a Picker four-circle automatic diffractometer. Zirconium-filtered Mo radiation (λ 0.7107 Å) was used to measure 2457 reflections ($2\theta_{\text{max}} = 45^\circ$) by the $\theta(\text{crystal}) - 2\theta(\text{counter})$ technique. The scan rate was 1°/min and the 2θ scan range was 1.5° plus the wavelength dispersion. Backgrounds of 15 s were measured before and after each scan.

A correction for crystal decomposition was made; the maximum correction was 9% in F_o . The data were also corrected for absorption effects using a six planar face model for the crystal. The minimum and maximum calculated transmission factors are 0.14 and 0.36, respectively. The linear absorption coefficient for Mo K α radiation is 61.3

cm^{-1} . Structure factor errors were estimated as previously described.²² Structure factors with $F_o < \sigma(F_o)$ were given zero weight in the refinements.

Structure Solution and Refinement. The structure was solved using "heavy-atom" techniques. Difficulties were encountered in the early stages of the structure solution because of pseudosymmetry resulting from the essentially zero value of the y coordinate of the Ta. The R value ($\sum(|F_o| - |F_c|)/\sum|F_o|$) was 0.062 with all nonhydrogen atoms included in the model with anisotropic temperature factors. All hydrogen atoms were observed in an electron density difference map at $0.3 \text{ e}/\text{\AA}^3$ for the benzyl and benzyldene, $0.2\text{--}0.4 \text{ e}/\text{\AA}^3$ for the phenyl, and $0.3\text{--}0.6 \text{ e}/\text{\AA}^3$ for the cyclopentadienyl hydrogens. All hydrogen atoms were included, but not refined, in calculated positions ($\text{C-H} = 1.0 \text{ \AA}$) with fixed isotropic temperature factors of 6.0 \AA^2 . Final refinements were done in two blocks: (a) the scale factor, tantalum, and C(1)–C(10) atoms; (b) the scale factor, tantalum, C(11)–C(17), and C(21)–C(27) atoms. The final R values for 1917 reflections with $F_o > \sigma(F_o)$ are 0.059 for R and 0.064 for $R_w[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Neutral atom scattering factors were used.²³ The Ta atom scattering factors were corrected for the real and imaginary parts of the anomalous scattering.²⁴ The function $\sum w(|F_o| - |F_c|)^2$ was minimized in the refinement.²⁵

The final positional and thermal parameters are given in Table II. A list of observed and calculated structure factors is available.²⁶

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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