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Preparation and Characterization of Tantalum(III) Olefin Complexes and Tantalum(V) Metallacyclopentane Complexes Made from Acyclic α Olefins

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Abstract: $TaCp(CHCMe_3)Cl_2$ (Cp = η^5-C_5H_5) reacts rapidly with ethylene and propylene to give the ethylene and propylene metallacyclopentane complexes, $CpCl_2TaCH_2CH_2CH_2CH_2$ and $CpCl_2TaCH_2CHMeCHMeCH_2$, respectively. Analogous Cp'' metallacyclopentane complexes (Cp'' = η^5-C_5Me_5) can be formed from (and are in equilibrium with) $TaCp''$(olefin)Cl_2 complexes and olefin (olefin = ethylene, propylene, 1-pentene, and neopentylethylene). The analogous styrene, *cis*-2-pentene, and cyclooctene complexes do not form observable metallacycles. A mixed ethylene/$RCH{=}CH_2$ metallacycle (R = e.g., methyl) can be observed on adding $RCH{=}CH_2$ to $TaCp''$(ethylene)Cl_2 at low temperatures. The configuration of $Cp''Cl_2TaCH_2CHRCHRCH_2$ is trans by ^{13}C NMR while a mixed metallacycle has two β-substituted isomers. Cp'' metallacycles decompose irreversibly by β-hydride elimination followed by reductive elimination to give primarily the 2,3-disubstituted 1-butene dimer. The dimer is displaced by the free olefin which is always present to give back the olefin complex quantitatively. The greater stability of the ethylene metallacycle compared to the propylene metallacycle toward β-elimination suggests that a β hydrogen bound to a tertiary carbon atom is abstracted more rapidly than one bound to a secondary carbon atom. A deuterium-labeling experiment has shown that D_α atoms do not scramble singly or pairwise in a hex-1-ene-*1,1-d2*/ethylene metallacycle before or during decomposition. This result has been used as evidence against degenerate olefin-metathesis-like methylene exchange in Ta metallacyclopentane complexes.

Introduction

Metallacyclopentane[2] complexes can be prepared from high-energy olefins such as norbornadiene,[3] 3,3-dimethylcyclopropene,[4] methylenecyclopropane,[4] butadiene,[5] or allene,[6] but simple α olefins or ethylene fail to give observable analogous metallacyclopentane complexes. A simple tetramethylene complex (for example) therefore must be prepared from a metal dihalide and the 1,4-di-Grignard or dilithiobutane[7] (or, more recently, $MgCH_2CH_2CH_2CH_2$[8]). Therefore we were surprised to find that Ta(V) metallacyclopentane complexes are the ultimate organometallic products when the neopentylidene ligand is cleaved from $TaCp(CHCMe_3)Cl_2$ by ordinary olefins such as ethylene or propylene,[9] or dienes such as 1,7-octadiene.[10] We now find that we can prepare a large class of similar metallacyclopentane complexes more simply from new α-olefin complexes of the type $Ta(\eta^5$-$C_5Me_5)$ (α-olefin)Cl_2. Since other workers have now shown that Zr(IV),[11] Ti(IV),[12] or Ni(II)[2c,12] metallacyclopentane complexes can also be prepared from simple olefins, this type of reaction may be more widespread than had heretofore been believed. The reason why such metallacycles have not been observed more commonly is due in part to the fact that they are normally not very stable. This is important since they can therefore be useful intermediates in catalytic processes.[10,12b,13]

In this paper we disclose full details of the preparation and characterization of monocyclopentadienyl dichlorotantalum(V) metallacyclopentane complexes made from olefins of the type $RCH{=}CH_2$ along with a study of how several decompose. How others decompose and how this type of complex can be used to selectively dimerize α olefins will be the subject of a subsequent paper.[14]

Results

η^5-C_5H_5 Metallacyclopentane Complexes (η^5-C_5H_5 = Cp). Orange $TaCp(CHCMe_3)Cl_2$[9] reacts rapidly with ethylene in pentane at 25 °C. The color first deepens to red, then lightens to yellow-orange as orange crystals of $CpCl_2TaCH_2CH_2CH_2CH_2$ (1) fall from solution in high yield (eq 1). The organic products of this reaction are Me_3C-
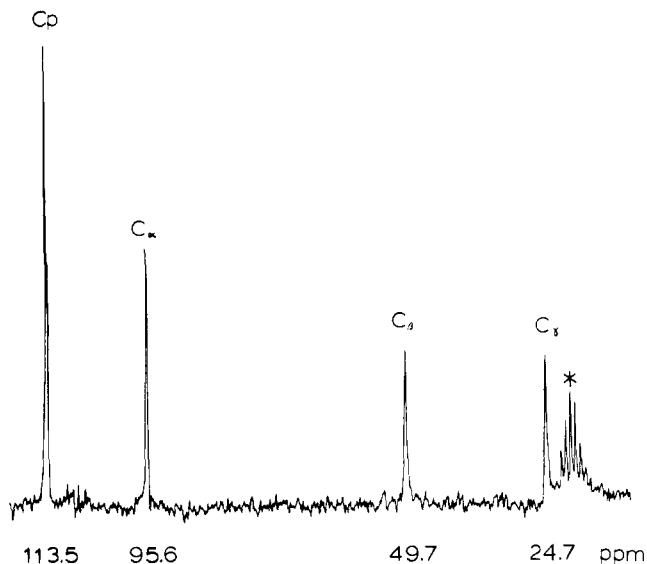
$TaCp(CHCMe_3)Cl_2 + 3C_2H_4$

$TaCp(CHCMe_3)Cl_2 + 3CH_3CH{=}CH_2$

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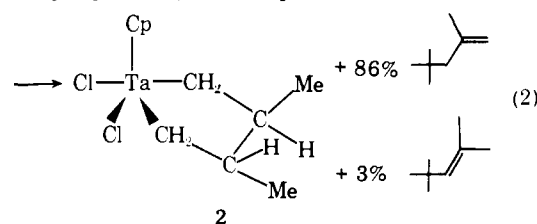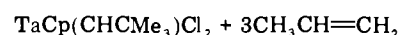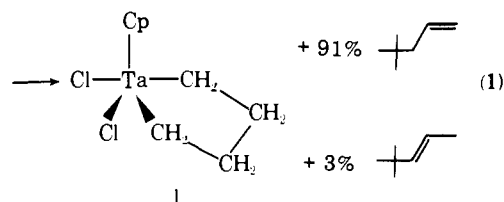
Figure 1. The 22.63-MHz $^{13}C\{^1H\}$ NMR spectrum of CpCl₂Ta$\overline{CH_2CH}$-MeCHMeCH₂ in toluene-d_8 (*) at 7 °C.

Figure 2. The 15.00-MHz $^{13}C\{^1H\}$ NMR spectrum of Cp″Cl₂-TaCH₂CHMeCHMeCH₂ in toluene-d_8 (*) at (a) −44 and (b) 0 °C. (c) An expansion of the CD₃C₆D₅, C$_\gamma$ and C$_\gamma'$ peaks at −44 °C.

CH₂CH=CH₂ (91% absolute yield) and *trans*-Me₃C-CH=CHMe (3%). Not a trace of Me₃CCH=CH₂ nor *tert*-butylcyclopropane was found. We observed a low-yield intermediate in this reaction by ^1H NMR at low temperatures (−78 to 0 °C) but had no means of identifying it; it disappeared on warming the sample to room temperature.

The corresponding reaction of TaCp(CHCMe₃)Cl₂ with propylene (50 psi) at 0 °C for 4 h gave CpCl₂TaCH₂CH-MeCHMeCH₂ (2) in high yield. The organic product mixture contained an 86% yield of Me₃CCH₂(CH₃)C=CH₂. Ta(η^5-C₅H₄Me)(CHCMe₃)Cl₂ reacted similarly with propylene at 0 °C in pentane to give a high yield of (η^5-C₅H₄Me)-Cl₂TaCH₂CHMeCHMeCH₂ (3).

The reaction between TaCp(CHCMe₃)Cl₂ and styrene overnight at 25 °C in benzene gave a 95% yield of *trans*-PhCH=CHCH₂CMe₃, but the brown, organometallic product was insoluble in common solvents. It could not be characterized. The reaction of NbCp(CHCMe₃)Cl₂ with ethylene gave 62% Me₃CCH₂=CH₂ and 2% *trans*-Me₃C-CH=CHCH₃ while reaction with propylene gave a 58% yield of Me₃CCH₂(CH₃)C=CH₂; again only an unidentifiable, paramagnetic, brown, organometallic product could be found. Similarly, Nb(η^5-C₅H₄Me)(CHCMe₃)Cl₂ reacted with ethylene to give an 87% yield of Me₃CCH₂CH=CH₂, but again apparently no stable niobium metallacycle.

The ethylene metallacycle (1) is sparingly soluble in pentane, but quite soluble in benzene or toluene. It darkens in the solid state at 25 °C under N₂ but remains orange under 600 mm of ethylene for several days. The solid-state decomposition under N₂ is very slow at −30 °C. In solution under an atmosphere of ethylene 1 is stable for at least 24 h at 25 °C. It is sensitive to water and oxygen.

The propylene metallacycle (2) is considerably less stable than 1. It decomposes in the solid state or in solution in about 1 h at 25 °C but is stable at −30 °C for several months.

The ^1H NMR spectrum of 1 under C₂H₄ is temperature dependent. At −40 °C four broad peaks are found at τ 6.35, 7.15, 7.95, and 8.10 (in addition to a single sharp cyclopenta-dienyl peak). These coalesce pairwise to give two overlapping broad peaks at τ 7.25 and 7.64 at 40 °C. Free ethylene does not exchange with coordinated ethylene at any point. An approximate $\Delta G^{\ddagger}$ (12.8 ± 0.8 kcal mol⁻¹) can be calculated employing either coalescing pair.

The gated decoupled ^{13}C NMR spectrum of 1 under ethylene at 25 °C shows a triplet at 90.1 ppm ($^1J_{CH}$ = 122 Hz),

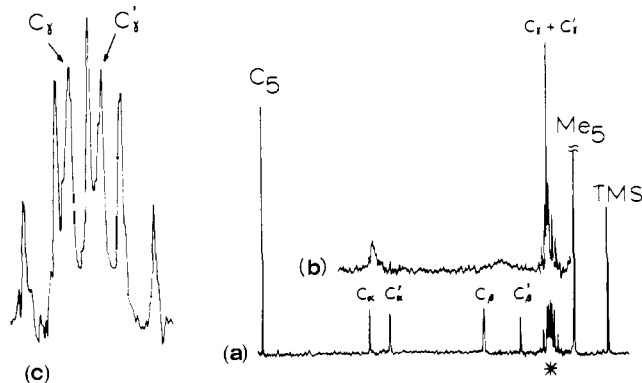a triplet at 34.0 ppm ($^1J_{CH}$ = 128 Hz), and a doublet at 113.3 ppm (J_{CH} = 174 Hz). The last is assigned to the cyclopenta-dienyl carbon atoms.[9] As we will see later on, the lower field triplet is most likely due to C$_\alpha$ and the higher field triplet due to C$_\beta$ in the metallacyclopentane ring. Either the temperature-dependent process observed in the ^1H NMR spectrum of 1 does not involve exchange of C$_\alpha$ with C$_\beta$, or the larger chemical-shift difference in the carbon spectrum prevents significant averaging of the two at 25 °C.
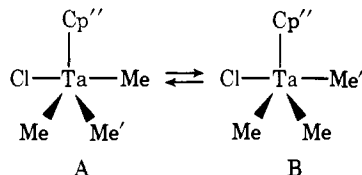
The 60-MHz ^1H NMR spectrum of 2 under propylene at 10 °C consists of a single sharp cyclopentadienyl resonance and a broad and complex pattern from τ ~7 to 9.5. Cooling the sample to −60 °C changes the shape of this complex pattern but it is still poorly resolved and not readily interpretable. The 270-MHz spectrum of analogous 3 at −10 °C shows four separate multiplets for the four protons on the C₅H₄Me ring. Therefore, the ground-state structure of 3 (and presumably also 2) does not contain a plane of symmetry; since the rate of the fluxional process is fast at this temperature a plane of symmetry is not created during the fluxional process.

The 22.63-MHz $^{13}C\{^1H\}$ NMR spectrum of 2 at 7 °C shows a single cyclopentadienyl carbon resonance at 113.5 ppm (J_{CH} = 181 Hz) but only three ring carbon atoms at 95.6 (t, J_{CH} = 123 Hz), 49.7 (d, J_{CH} = 126 Hz), and 24.7 ppm (q, J_{CH} = 128 Hz) due respectively to C$_\alpha$, C$_\beta$, and C$_\gamma$ type carbon atoms (Figure 1). (The coupling constants were determined from a 67.89-MHz gated decoupled spectrum at 10 °C.) Since the molecule does not contain a plane of symmetry (vide supra) a fluxional process must be interconverting C$_\alpha$ and C$_\alpha'$, C$_\beta$ and C$_\beta'$, and C$_\gamma$ and C$_\gamma'$ in the unsymmetric ground-state molecule. This can be shown by cooling the sample to −35 °C, where-upon the C$_\beta$ and C$_\beta'$ and C$_\gamma$ and C$_\gamma'$ peaks can be found at 51.4, 48.5, 27.1, and 23.6 ppm, respectively; C$_\alpha$ and C$_\alpha'$ must be accidentally coincident since the C$_\alpha$ peak remains sharp along with that due to the cyclopentadienyl carbon atom. (Note that the C$_\alpha$ and C$_\alpha'$ signals in the corresponding η^5-C₅Me₅ complex are not coincident at low temperature; Figure 2 and see later.) If we assume that the molecule is a pseudo-tetrag-onal pyramid (see Discussion), the only reasonable description of the asymmetric ground state is one containing a *trans*-β,β'-dimethylmetallacyclopentane ring. We have no ^{13}C evidence for *cis*-β,β'-2 or *cis*- or *trans*-α,β'-2. The fluxional process therefore must consist of a pseudorotation which takes

trans-β,β'-2
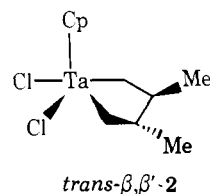
C_α into C_α', C_β into C_β', and C_γ into C_γ'. $\Delta G^\pm$ for this process at 258 K = 11.8 ± 0.5 kcal mol^{-1}. A similar process must occur in **1**.

We can demonstrate that this type of pseudorotation process occurs readily for other Ta monocyclopentadienyl compounds which are not metallacycles. The room temperature 270-MHz ^{1}H NMR spectrum of TaCp″Me₃Cl (Cp″ = η^5-C₅Me₅) shows only one methyl peak at τ 9.10. At −40 °C this divides into two in a 1:2 ratio at τ 9.12 and 9.14, respectively. The 15.00-MHz ^{13}C NMR spectrum of this molecule is likewise temperature dependent. At −78 °C two methyl groups of one type give rise to one peak at τ 73.1 and a third to a peak about one-half its size at τ 71.5. At 30 °C there is a single signal at 72.8 ppm for all three methyl groups. Each of the low-temperature spectra is consistent with a ground-state structure A which at higher temperature interconverts with B, thereby eventually scram-

bling all methyl groups. $\Delta G^\pm$ for this process calculated from ^{1}H NMR spectra is 13.6 ± 1.4 kcal mol^{-1}, a value which we believe to be characteristic of a pseudorotation process in tetragonal pyramidal Ta(V) monocyclopentadienyl complexes. This type of process is, of course, well-known in organometallic chemistry. (See, for example, studies of monocyclopentadienyl complexes of Mo.[15])

η^5-C₅Me₅ Olefin Complexes. We believed that Ta(III) olefin complexes, TaCp(olefin)Cl₂, might provide an easier and more general route to **1** and **2**. However, we saw no evidence of stable species of this type when **1** or **2** decomposed. (Loss of a component olefin from other transition metal metallacyclopentane complexes is well documented.[7,12]) Since we believed that they might decompose bimolecularly, we attempted to prepare the analogous η^5-C₅Me₅ complexes, in which bimolecular decomposition would be less likely. Complications caused by addition of a cyclopentadienyl C–H bond to the metal would also be eliminated.[16] This route to Cp″ metallacycles would be especially valuable since TaCp″(CHCMe₃)Cl₂ cannot be prepared easily or in any reasonable quantity from TaCp″-(CH₂CMe₃)₂Cl₂.[18]

The reaction between TaCp″(CH₂CMe₃)Cl₃[18] and slightly more than 0.5 equiv of ZnEt₂ in toluene at −78 °C, followed by warming to 25 °C, gives red **4** in 50% isolated yield:

TaCp″(CH₂CMe₃)Cl₃ + ½ZnEt₂
$\rightarrow$ TaCp″(CH₂CMe₃)(C₂H₅)Cl₂

$\xrightarrow{-CMe_4}$ TaCp″(C₂H₄)Cl₂ (**4**)   (3)
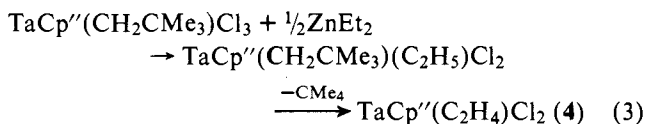
The presumed intermediate, TaCp″(CH₂CMe₃)(C₂H₅)Cl₂, is apparently unstable at 25 °C and decomposes by losing neopentane. An analogous reaction of TaCp″(CH₂CMe₃)Cl₃ with 0.5 equiv of ZnPr₂ gave red-purple TaCp″(propylene)Cl₂ (**5**) in 75% isolated yield:

TaCp″(CH₂CMe₃)Cl₃ + ½ZnPr₂
$\xrightarrow{-CMe_4}$ TaCp″(propylene)Cl₂ (**5**)   (4)
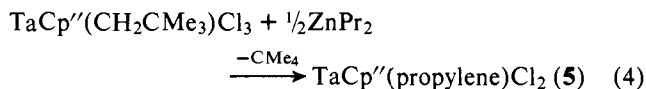
Styrene reacts with **4** at 70 °C in 1 h to give TaCp″(styrene)Cl₂ (**6**, Scheme I). A similar reaction of styrene with **5** gives **6** in high yield at 25 °C in 24 h. Therefore, **5** is a good precursor for preparing similar 1-pentene, *cis*-2-pentene, cyclooctene, and neopentylethylene complexes (**7, 8, 9,** and **10**, respectively) in high yield (Scheme I). (Most of the fundamental reactions of metallacycles and their olefin complexes

Scheme I
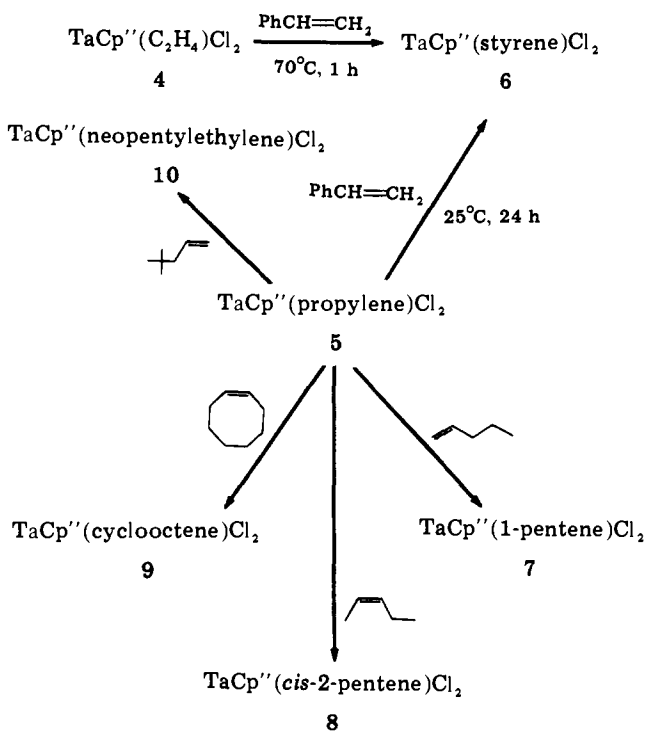
are found in this deceptively simple set of reactions. Therefore we must put off discussing details until the last Results section.)

The reaction between **5** and *trans*-2-pentene is anomalous. The only identifiable product after 24 h at 25 °C was the 1-pentene complex in 22% yield (eq 5). Much pentane-insoluble brown material was formed which had no ^{1}H NMR spectrum. A similar attempt to prepare an isobutylene complex gave no identifiable new organometallic species and much brown precipitate. Evidently both the *trans*-2-pentene and isobutylene complexes are unstable at 25 °C.

TaCp(propylene)Cl₂ + *trans*-2-pentene
$\rightarrow$ TaCp″(1-pentene)Cl₂ (**7**) (22% yield)   (5)
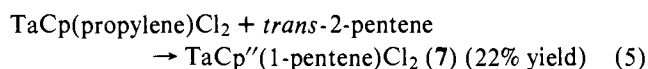
All of the above olefin complexes are nicely crystalline. The ethylene (**4**), styrene (**6**), and cyclooctene (**9**) complexes are only slightly soluble in pentane but the others are nicely soluble. All are extremely sensitive to oxygen and moisture in solution and not very stable thermally; for example, **5** decomposes completely in 30 min in chlorobenzene at 95 °C to give a sparingly soluble, green, crystalline product in moderate yield. It analyzes (C, H, and Cl) as TaCp″Cl₃ and forms a red, crystalline adduct with one PMe₃ which has an eight-line EPR spectrum at g = 1.88 in chlorobenzene at 298 K consistent with TaCp″Cl₃(PMe₃). TaCp″Cl₃(PMe₃) is oxidized to TaCp″-Cl₄(PMe₃) rapidly at room temperature in chloroform.

The ^{1}H NMR spectrum of **4** in C₆D₆ at 25 °C consists of two singlets due to η^5-C₅Me₅ and ethylene at τ 8.37 and 7.62, respectively. On cooling the sample, the latter resonance collapses into two broad singlets characteristic of a nonrotating ethylene ligand. $\Delta G^\pm$ for this process is 9.3 ± 0.3 kcal mol^{-1}. The ^{1}H NMR spectrum of every other olefin complex is considerably more complex owing to the asymmetry of these molecules.

The gated decoupled ^{13}C NMR spectrum of each olefin complex is unambiguous. All multiplicities and $^1J_{CH}$ coupling constants are those expected; sp^3 carbon-H coupling constants vary from about 124 to 129 Hz while olefinic carbon-H coupling constants vary from 142 to 152 Hz.

All attempts to prepare η^5-C₅H₅ compounds analogous to **4–10** by similar techniques failed. Evidently such complexes,

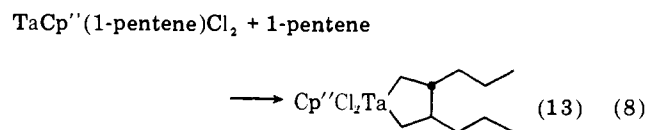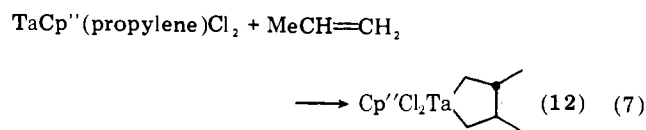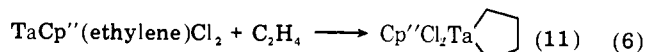**Table I.** ^{13}C NMR Chemical Shifts in Tantalacyclopentane Complexes[a]

compd	t, °C	α	β	other	C₅R₅	$\Delta G^{\ddagger}$ for pseudorotation, kcal mol⁻¹ (K)
CpCl₂TaCH₂CH₂CH₂CH₂[d]	25[b]	90.1	34.0		113.3	12.8 ± 0.8 (258)
CpCl₂TaCH₂CHMeCHMeCH₂[e]	−35[b]	96.4	51.4	27.1, γ	113.2	11.8 ± 0.5 (258)
			48.5	23.6, γ'		
Cp''Cl₂TaCH₂CH₂CH₂CH₂	−3[c]	78.7	22.5		12.0,	13.0 ± 0.4 (270)
					122.5	
Cp''Cl₂TaCH₂CHMeCHMeCH₂[f]	−44[c]	84.9	44.3	21.2, γ	12.1	11.9 ± 0.4 (251)
		77.7	31.4	19.9, γ'	122.7	
Cp''Cl₂TaCH₂CH(n-Pr)CH(n-Pr)CH₂[g]	−40[b]	82.1		15.1, 15.2, 20.9, 22.4	12.1	
		73.6		34.1, 37.0, 37.7, 46.9	122.6	
Cp''Cl₂TaCH₂CHMeCH₂CH₂[h,i]	−35[b]	72.8, α(A)	30.4, β(B)	26.9, γ(D)	12.0 (F)	
		83.5, α(E)	25.8, β(C)	38.8, γ(d)	12.2 (f)	
		81.5, α(a)	31.4, β(b)		122.4 (G)	
		86.9, α(e)	25.6, β(c)		123.0 (g)	
Cp''Cl₂TaCH₂CH(n-Bu)CH₂CH₂	−46[c]	72.4, α(A)[i]		14.7, 23.6, 28.5	12.0	
		81.6, α(E)[j]		29.7, 30.3, 41.6	122.3	

[a] Chemical shifts are in parts per million downfield of Me₄Si. Solvent = C₆D₆ or toluene-d_8. Peak assignments are based on chemical shifts (carbon atoms bonded directly to Ta are shifted downfield), multiplicities in the ^1H gated decoupled spectra, and coalescence patterns due to pseudorotation. [b] 67.89 MHz. [c] 15.00 MHz. [d] $^1J_{CH}$ (Hz): α (122), β (128), C₅H₅ (174). [e] $^1J_{CH}$ (Hz): α (123), β (126), γ (128), C₅H₅ (181). [f] $^1J_{CH}$ (Hz): α (125), α' (135). [g] $^1J_{CH}$ (Hz): α (132), α' (124). [h] $^1J_{CH}$ (Hz): α (A), 130; α (E), 132; α (a), 124; α (e), 124; β (B), 127; β (C), 122; γ (D), 128; γ (d), 121; C₅Me₅ (F), 129; C₅Me₅ (f), 129. [i] Refer to Figure 3 for the labeling sequence in the two β-substituted isomers. [j] This peak is absent in the corresponding spectrum of the 1-hexene-$1,1$-d_2 complex.

as originally suspected, are not stable, either because bimolecular decomposition pathways are not sterically blocked and/or because cyclopentadienyl carbon–hydrogen bonds are cleaved in the decomposition process. Unfortunately, we have also been unsuccessful in our attempts to prepare NbCp''-(olefin)Cl₂ complexes by the β-elimination route[19] and NbCp''(CHCMe₃)Cl₂ is unknown.[18] The only known Nb metallacycle, the "benzometallacyclopentene" complex, Cp''Me₂NbCH₂CH₂C₆H₄,[20] is stable at 25 °C.

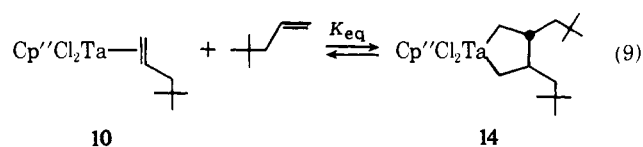**η^5-C₅Me₅ Metallacyclopentane Complexes.** TaCp''-(C₂H₄)Cl₂ reacts instantly with ethylene, even at −35 °C, to give orange Cp''Cl₂TaCH₂CH₂CH₂CH₂ (**11**); it can be isolated easily and is fairly stable at 25 °C (eq 6). The propylene and 1-pentene metallacycles (**12** and **13**; eq 7 and 8) can be

$$TaCp''(ethylene)Cl_2 + C_2H_4 \longrightarrow Cp''Cl_2Ta\!\!\big< \quad (11) \quad (6)$$

$$TaCp''(propylene)Cl_2 + MeCH{=}CH_2$$
$$\longrightarrow Cp''Cl_2Ta\!\!\big< \quad (12) \quad (7)$$

$$TaCp''(1{\text -}pentene)Cl_2 + 1{\text -}pentene$$
$$\longrightarrow Cp''Cl_2Ta\!\!\big< \quad (13) \quad (8)$$

prepared analogously from the propylene and 1-pentene complexes, respectively, but they must be isolated at 0 °C to prevent decomposition. The general physical properties of **11** are similar to those of **1** and those of **12** and **13** are similar to those of **2**.

The variable-temperature ^1H and ^{13}C NMR spectra of **11–13** differ little from those of their η^5-C₅H₅ counterparts. For example, the low-temperature ^{13}C NMR spectrum of **12** (Figure 2) show six different ring carbon resonances and one set of Cp'' resonances, consistent with an asymmetric molecule; since the low-field pair due to C_α and $C_{\alpha'}$ in the ring are triplets in the gated decoupled ^{13}C NMR spectrum, it must be the β,β'-disubstituted isomer. Some $\Delta G^{\ddagger}$ values for pseudorotations along with ^{13}C NMR shifts for all metallacyclopentane complexes are collected in Table I.

The purple color of a solution of TaCp''(neopentylethylene)Cl₂ (**10**) does *not* immediately change to the orange color characteristic of a metallacycle when excess neopentylethylene is added at 0 °C. Slowly (in 2 h) the purple color does begin to fade, but not completely to orange, irrespective of the time elapsed. A ^{13}C NMR spectrum of a sample (∼1 M) which had been equilibrated with 4 equiv of neopentylethylene at 0 °C for 24 h showed it to be a ca. 1:3 mixture of the starting material (**10**) and one neopentylethylene metallacycle complex. The two signals for the α-carbon atoms at δ 79.1 and 88.4 are triplets (J_{CH} = 127 and 128 Hz, respectively) in the gated decoupled spectrum. Therefore this metallacycle must be β,β'-disubstituted **14**. From the above data (assuming that equilibration is complete in 24 h at 0 °C) we can estimate that $K_{eq} \approx 1.5$ at 0 °C for **10** ⇌ **14** (eq 9).

$$Cp''Cl_2Ta{-}\big| + \diagup{=} \underset{\longleftarrow}{\overset{K_{eq}}{\rightleftharpoons}} Cp''Cl_2Ta\!\!\big< \quad (9)$$

10   **14**

We can assume that all metallacycles are in equilibrium with an olefin complex and free olefin since even **11** easily reverts to **4** and ethylene in toluene at 25 °C when a slight vacuum is applied above the solution or the atmosphere is steadily purged. However, we note again that the rate of this reversible metallacycle formation is not fast enough to observe by NMR methods and also that the equilibrium must lie well toward **11** (cf. **10** ⇌ **14**).

Under no conditions have we been able to observe a styrene metallacycle prepared from TaCp''(styrene)Cl₂ (**6**) and excess styrene. The color of the solution remains purple (characteristic of **6**) at all temperatures and only **6** can be seen in the ^1H NMR spectrum. We do have evidence that styrene will attack **6** rapidly, however. On adding excess PhCH=CD₂ to **6**, TaCp''(PhCH=CD₂)Cl₂ and PhCH=CH₂ are generated within 10 min at 25 °C according to the ^1H NMR spectrum of the mixture (eq 10). Note that the olefins could exchange without first forming a metallacycle. We will present other evidence below which supports this contention.

$$TaCp''(PhCH{=}CH_2)Cl_2 + excess\ PhCH{=}CD_2$$
$$\rightarrow TaCp''(PhCH{=}CD_2)Cl_2 + PhCH{=}CH_2 \quad (10)$$

Figure 3. The 67.89-MHz $^{13}C\{^1H\}$ NMR spectrum of $Cp''Cl_2$-$TaCH_2CHMeCH_2CH_2$ in toluene-d_8 (*) at -35 °C. Capital letters refer to carbon atoms in the major isomer, lower case letters to those in the minor isomer according to the figure (X = free propylene). The assignments are based on CH coupling and by comparison with the $^{13}C\{^1H\}$ NMR spectrum of the mixed metallocycle formed from **4** and hex-1-ene-$1,1$-d_2 (see Table I).

$TaCp''(cis$-2-pentene$)Cl_2$ does not add cis-2-pentene to form a metallacycle according to a ^1H NMR spectrum of the mixture.

Ethylene/Olefin' Metallacyclopentane Complexes and the Absence of Deuterium Scrambling before Decomposition. When 1 mol of propylene is added to $TaCp''(C_2H_4)Cl_2$ at -35 °C the orange mixed metallacycle **15** (eq 11) is generated

4

15a

11   **15b**

quantitatively. At low temperatures the $^{13}C\{^1H\}$ NMR spectrum shows two β-substituted isomers (the four C_α resonances are all triplets in the gated decoupled spectrum) in a ratio of about 5:1 (Figure 3 and Table I). These interconvert by pseudorotation on the NMR time scale at 0 °C but the high-temperature limit cannot be reached before irreversible changes ensue.

After the sample of **15** was warmed to 10 °C for 2 h and cooled again to -40 °C the ^{13}C NMR spectrum showed that only about 50% of **15** remained; the rest was a 1:1 mixture of the ethylene metallacycle (**11**) and the propylene metallacycle (**12**, eq 12). This finding is consistent with earlier results. **15**

15   **11**   **12**

gives **4** (by losing propylene) or **5** (by losing ethylene); **4** and **5** then capture free ethylene or propylene (respectively) to give **11** and **12** (respectively).

The corresponding reaction of $TaCp''(propylene)Cl_2$ (**5**) with 1 mol of ethylene at -45 °C is much more complex. Not all the starting material is consumed. The major new product is $TaCp''(C_2H_4)Cl_2$ with lesser amounts of the ethylene me-

5

11   **12**

tallacycle and the propylene metallacycle being formed (eq 13). We could see no **15**. Since at -45 °C (1) **15** would be stable toward olefin scrambling to give **11** or **12**, (2) **15** does not react with ethylene, and (3) loss of propylene from **5** to give the 12-electron $TaCp''Cl_2$ fragment seems unlikely, ethylene must displace propylene without forming a metallacycle (cf. styrene exchange above).

1-Hexene reacts with **4** to give only one mixed metallacycle which by ^{13}C NMR is analogous to one of those obtained with propylene. By using hex-1-ene-$1,1$-d_2[21] we can show that one C_α in the major isomer has deuterium bound to it (**16**, see Table I) and that this species is configurationally stable in the sense that deuterium does not scramble singly or pairwise (most importantly to give **16'**) in 24 h at 0 °C (eq 14). Upon

16   **16'** (14)

warming a sample of **16** it begins to disproportionate (like **15**) to **11** and the hex-1-ene-$1,1$-d_2 metallacycle.

$TaCp''(C_2H_4)Cl_2$ (**4**) reacts with 1.2 mol of styrene at -35 °C in toluene-d_8 to give **6** and **11** (eq 15) in the time needed to

$$TaCp''(C_2H_4)Cl_2 \xrightarrow[\text{1.2 styrene}]{-35\ ^\circ C} 0.5 TaCp''(styrene)Cl_2$$

4   **6**

11

observe the $^{13}C\{^1H\}$ NMR spectrum ($\sim$0.5 h). There is no way of knowing whether an ethylene/styrene metallacycle was an intermediate, but in view of the ease of forming other ethylene/olefin' metallacycles such as **16** at -35 °C we would suspect that it was not. Styrene simply displaces ethylene, which is then rapidly scavenged by **4** to give **11**.

We conclude that ethylene/olefin' metallacycles, if formed, will always disproportionate. The reaction appears to be driven by formation of **11**; of all equilibria, that between **4** and ethylene to give **11** lies furthest to the right, and it is most rapidly attained. Almost certainly, therefore, ethylene/olefin' metallacycles will be a special case of the more general class of olefin/olefin' mixed metallacycles (see later).

Decomposition of $Cp''Cl_2TaCH_2CHMeCHMeCH_2$. All η^5-C_5Me_5 metallacyclopentane complexes decompose to the corresponding olefin complexes in solution at 25 °C in 24 h *in an open system*. One means of accomplishing this transformation is to cleave the β,β'-carbon bond and lose 1 mol of olefin from the metallacycle. This is always occurring at a fairly rapid rate, even when the olefin is ethylene, and is especially facile when the olefin is substituted with a bulky group (e.g., neopentyl). However, in a closed system the ethylene metallacycle is comparatively stable while the substituted metallacycles still decompose readily to the corresponding olefin complexes. Therefore an olefin complex must be able to form another way. We will examine the propylene and the ethylene/olefin' metallacycles in detail as they are suitable models for all others.

The orange propylene metallacycle (**12**) decomposes smoothly in benzene at 25 °C to give 0.5 mol per tantalum of 2,3-dimethyl-1-butene, traces ($\sim$0.003 per Ta) of (inter alia) 2-methyl-1-pentene, and the purple propylene complex (**5**) quantitatively. The rate of disappearance of $Cp''Cl_2TaCH_2CHMeCHMeCH_2$ is first order by NMR with

Scheme II

$\Delta H^{\ddagger} = 18.3 \pm 1.2 \text{ kcal mol}^{-1}$ and $\Delta S^{\ddagger} = -15 \pm 4$ eu. (Since these values within experimental error are the same as those for the catalytic reaction[14] they depend little on propylene concentration; therefore the equilibrium must lie well toward the metallacycle.) By GC the rate of appearance of 2,3-dimethyl-1-butene is also first order and at 31.5 °C is half the rate at which **12** disappears in the first experiment.

Scheme II is consistent with these results. We propose that the major product forms via the steps A–C. We can safely predict that step C will not be rate determining but cannot from this data differentiate between A and B as the rate-determining step (see Discussion). If we call k_1 the rate constant for the sum of the steps A and B and assume that step C will be relatively fast, then the observed rate constant is $2k_1$ for disappearance of **12** by ^{1}H NMR; at 31.5 °C $k_1(\mathbf{12}) = 0.014 \pm 0.001 \text{ min}^{-1}$. By GC (the appearance of 2,3-dimethyl-1-butene) $k_1 = 0.012 \pm 0.002 \text{ min}^{-1}$.

$\text{CpCl}_2\text{TaCH}_2\text{CHMeCHMeCH}_2$ (**2**) decomposes in solution analogously to give 0.5 mol of 2,3-dimethyl-1-butene. The first-order rate constant for decomposition of **2** is twice that for decomposition of **12** ($0.023 \pm 0.003 \text{ min}^{-1}$ for **2** vs. 0.012 min^{-1} for **12** at 31.5 °C). TaCp(propylene)Cl$_2$ must decompose more readily than TaCp''(propylene)Cl$_2$ at this temperature and is never observed. (As we noted earlier, we could not prepare TaCp(olefin)Cl$_2$ complexes by the route used to prepare the Cp'' analogues.)

We should note that the Cp and Cp'' ethylene metallacycles do not decompose at a similar rate until about 70 °C. It seems plausible to propose that a β hydrogen is abstracted much more readily from a tertiary β-carbon atom than a secondary one. There are, however, inherent difficulties in providing this as will be pointed out in the Discussion section.

**Decomposition of Cp''Cl$_2$TaCH$_2$CH$_2$CHRCH$_2$.** The ethylene/propylene metallacycle (**15**, eq 12) first disproportionates to the ethylene metallacycle and the propylene metallacycle (eq 16). After warming to 52 °C for 30 min the only

(4:5 = 5:1)
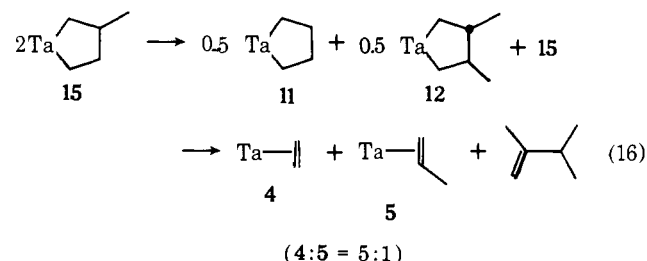
identifiable organometallic compounds were the ethylene complex and propylene complex in a ratio of 5:1. The only major organic product observed by ^{1}H or ^{13}C NMR or GC analysis was 2,3-dimethyl-1-butene; none of the mixed dimer could be detected. Apparently olefin scrambling to give **11** and **12** is fast. **11** is stable toward β-elimination under these conditions and only serves as a source of ethylene and **4**. More **4** is formed since any **5** reacts with ethylene to give largely **4** (vide supra).

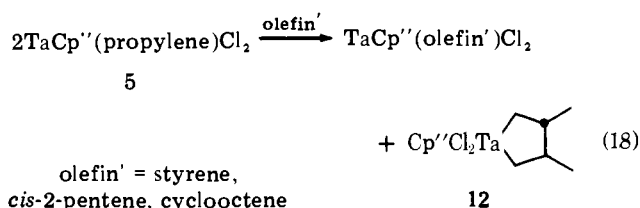The ethylene/1-hexene "mixed" metallacycle similarly decomposes to the ethylene complex and an analogous 2,3-

disubstituted 1-butene. (2,3-Disubstituted 1-butenes are more easily prepared and identified via the catalytic dimerization reaction[14] so a full proof of the identity of such species will be presented at that time.) The 2-butyl-3-methyl-1-heptene formed when the corresponding ethylene/hex-1-ene-*1,1-d$_2$* metallacycle (**16**) decomposes was shown to be >98% $\text{C}_{12}\text{H}_{20}\text{D}_4$ by mass spectroscopy (eq 17). We conclude that

$\longrightarrow \text{C}_{12}\text{H}_{20}\text{D}_4$ (17)
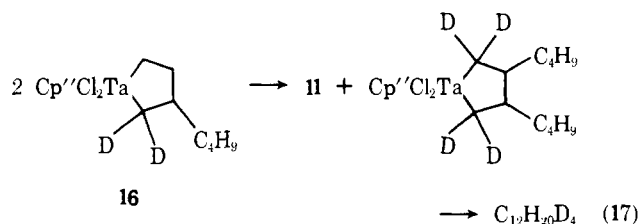
deuterium scrambling into the ethylene component of **16** during decomposition is negligible.[22]

On the Formation and Decomposition of Olefin/Olefin' Metallacyclopentane Complexes. We are now in a position to understand some of the first ostensibly simple reactions which we presented in Scheme I.

In the reaction of **5** with styrene, *cis*-2-pentene, and cyclooctene, the only organic product observed by ^{1}H NMR is 2,3-dimethyl-1-butene. **12** must form initially (eq 18) and then

$$2\text{TaCp}''(\text{propylene})\text{Cl}_2 \xrightarrow{\text{olefin}'} \text{TaCp}''(\text{olefin}')\text{Cl}_2$$

5

olefin' = styrene,
cis-2-pentene, cyclooctene   **12**

decompose to a 2,3-dimethyl-1-butene complex. The coordinated 2,3-dimethyl-1-butene can be displaced easily by the excess olefin' present in solution and TaCp''(olefin')Cl$_2$ is formed virtually quantitatively. Consistent with this proposal, we are able to observe the propylene metallacycle (**12**) by ^{1}H NMR early in the reaction. Either there is little or no propylene/olefin' metallacycle formed with these olefins (see Experimental Section) or the rate of β-elimination from such a mixed metallacycle is slow relative to loss of an olefin.
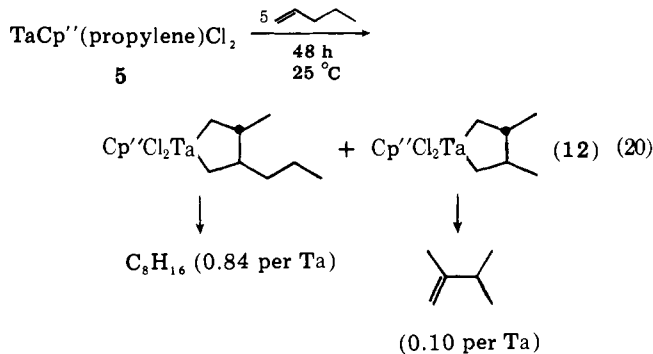
The reaction of **5** with neopentylethylene is more complex. Only ca. 65% of the initial propylene ends up in 2,3-dimethyl-1-butene. The remainder is found in codimers of propylene and neopentylethylene (two major isomers, parent ions $\text{C}_{10}\text{H}_{20}$ by GC/mass spectrum). We propose that these products form primarily from a propylene/neopentylethylene mixed metallacycle, e.g., that shown in eq 19. (The total pro-

(0.34 per Ta)
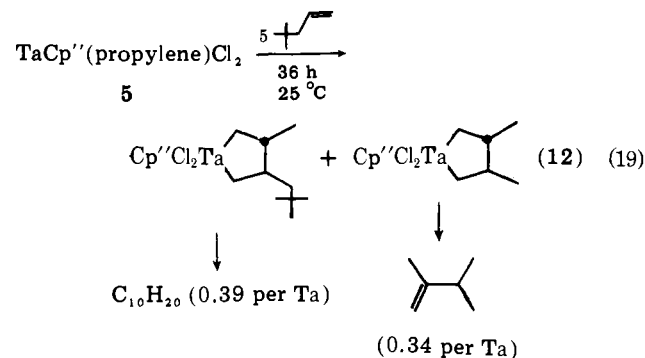
pylene in the products is 1.07 per Ta, rather than 1.00, owing to the usual experimental errors in determining absolute yields.)

The analogous reaction of **5** with 1-pentene gives only 0.10 equiv of 2,3-dimethyl-1-butene. *Most* of the propylene appears

in two codimers of empirical formula C_8H_{16} (0.84 per Ta). We propose that these codimers form primarily from the mixed metallacycle shown in eq 20.

$$TaCp''(\text{propylene})Cl_2 \xrightarrow[\substack{48\ h \\ 25\ ^\circ C}]{5\ \wedge\wedge\wedge}$$

5

$$Cp''Cl_2Ta\langle\rangle + Cp''Cl_2Ta\langle\rangle \quad (12)\quad (20)$$

$$C_8H_{16}\ (0.84\ \text{per Ta}) \qquad\qquad (0.10\ \text{per Ta})$$

What is unclear at this time is how much of the added olefin displaces propylene directly from **5** and how much adds to give the mixed metallacycle. Therefore we do not know how much **12** forms from displaced propylene (and **5**) and how much forms by scrambling of the mixed metallacycle before it decomposes to mixed dimer.

Discussion

Recent X-ray results show that the axis formed by the carbon–carbon bond of the ethylene in $TaCp''(C_2H_4)Cl_2$ lies parallel to the Cp'' ring.[23] This is the expected orientation since we now know that the plane of the neopentylidene ligand in $TaCp(CHCMe_3)Cl_2$ is perpendicular to the Cp ring[24] and olefins and alkylidenes are oriented 90° apart in biscyclopentadienyl complexes such as $TaCp_2(C_2H_4)(CH_3)$ and $TaCp_2(CH_2)(CH_3)$.[25] This orthogonal relationship apparently holds for complexes with other d^n configurations, e.g., tetramethylallene bonds parallel in $_1[FeCp(CO)_2(\text{tetramethylallene})]^+$ [26] while the dimethylmethylene ligand in $MnCp(CO)_2(CMe_2)$ bonds perpendicular to the Cp ring.[27] The reason why $TaCp''(\text{isobutylene})Cl_2$ and $TaCp''(\text{trans-2-pentene})Cl_2$ are not isolable therefore could be due in part to the fact that these olefins cannot easily lie parallel to the Cp'' ring without one substituent interacting with the ring (cf. $[FeCp(CO)_2(\text{olefin})]^+$ complexes[28]).

The only other d^2 olefin complexes are members of the $MCp_2(C_2H_4)X$ family (M = Nb or Ta; X = Et,[29] H,[29] I,[25] CH_3[25]). Ethylene does not rotate in these complexes, even on the chemical time scale,[25] since there is no π-bonding orbital of suitable energy perpendicular to that which is used, and because such rotation would be difficult for steric reasons.[25,29b] Evidently neither is true of complexes of the type $TaCp''(\text{olefin})Cl_2$, at least when the olefin is relatively small (e.g., ethylene). Larger, substituted olefins may only be able to "oscillate" about the Ta–olefin bond.[28]

An incoming olefin may prefer to approach the metal in an olefin complex from below along a line coincident with that between Ta and the center of the Cp'' ring. This position seems most accessible sterically. If a metallacycle (B, Scheme III) forms from this bisolefin complex (A), it would be the transition state in pseudorotation of a tetragonal pyramidal metallacyclopentane complex, C. At present we cannot eliminate other modes of attack, the two most likely being a trans attack to give D or a cis attack to give F. Either actually would be a more direct way of exchanging olefins (to give E) without forming a metallacycle.

An X-ray structure of a stable Pt tetramethylene complex shows a C_α–Pt–C_α bond angle of 80°.[7a] In $TaCp''Cl(CPh)(PMe_3)_2$, an almost perfect $TaCp''L_4$ tetragonal pyramid, the average L–Ta–L bond angle is $80 \pm 1°$.[30] Therefore, C (Scheme III) would seem the most likely structure for the metallacyclopentane complexes being discussed here. We

Scheme III
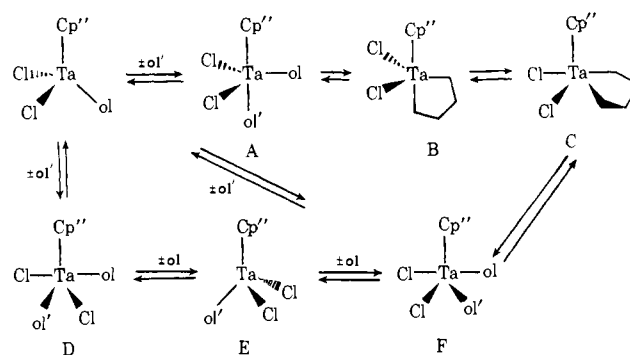
might assume that the TaC_4 ring will not be strictly planar, but puckered like the PtC_4 ring,[7a] especially if substituted. Puckering could assist the pseudorotation process (C $\rightleftarrows$ B) and also is almost certainly necessary in order for a β-hydride to transfer to the metal.

The location of substituents on the TaC_4 ring is probably determined largely by steric factors. Apparently the β,β'-disubstituted ring ("diaxial" or "diequatorial" if the TaC_4 ring is significantly puckered) is favored. Grubbs'[12a] finding that the predominant titanocene propylene metallacycle is α,α' substituted is especially interesting in view of the above results but it should be noted that ordinary, less sterically demanding η^5-C_5H_5 rings are present. Similar decamethylzirconocene metallacycles are again predominantly trans β,β' disubstituted.[11]

We have not yet demonstrated what is possibly the next lowest energy step after pseudorotation in a metallacycle, breakup of the ring without loss of olefin.[12b] It is an entirely logical step prior to loss of one olefin and we do have good evidence that some bisolefin complex is an intermediate in the olefin exchange reaction. It is interesting to speculate, however, whether C $\rightarrow$ F (Scheme III) or B $\rightarrow$ A is the preferred mode of cleavage. There is good evidence that the geometry, as well as the coordination number, is an integral part of the cleavage process in nickel metallacycles.[2c,7d]

The first readily observable higher energy process after pseudorotation is loss of one olefin to give the olefin complex. We have only qualitative data concerning the equilibrium between the metallacycle and the olefin complex. What we have seen, however, is fully in accord with what one might expect; an α olefin with a smaller substituent forms a metallacycle more readily and completely. Quantitative data are more easily obtained in the presence of excess olefin and therefore will be reported in the next paper.[14]

The next highest energy process is rearrangement of the metallacycle to a new olefin. As postulated in Scheme II, the rearrangment almost certainly consists of two steps, β-hydride elimination to give a butenyl hydride complex (step A) and transfer of that hydride to the butenyl α-carbon atom to give the new olefin (step B). The widely differing stabilities of $Cp''Cl_2TaCH_2CH_2CH_2CH_2$, $Cp''Cl_2TaCH_2CHRCHRCH_2$, and metallabicyclic complexes made from dienes[10] would seem to suggest that "step A is rate determining". This is not necessarily true since, although k_B will probably not change too much from one case to another, k_A(forward) and k_A(reverse) will. Both their relative and absolute magnitudes will determine how fast step A is relative to step B.[31]

The decomposition of **16** was studied in order to determine if degenerate olefin metathesis-like methylene exchange (**16** $\rightarrow$ **16'**, eq 14) occurs during decomposition, since metallacyclopentane complexes are still plausible intermediates in olefin metathesis,[7a,34,35] degenerate methylene exchange is the fastest form of metathesis,[34] and Ta(V) metallacycles are closely related to the unstable W(VI) metallacycles in which such

scrambling has been observed.[35] Since it does not, **16** must disproportionate to **11** and the 1-hexene-*1,1-d₂* metallacycle at a rate which is fast relative to methylene exchange. We did not attempt double-labeling experiments in metallacycles such as **17** in order to show that methylenes also do not scramble in

17

18

$$\text{etc.} \quad (21)$$

olefin rotation

(* = ¹³C)
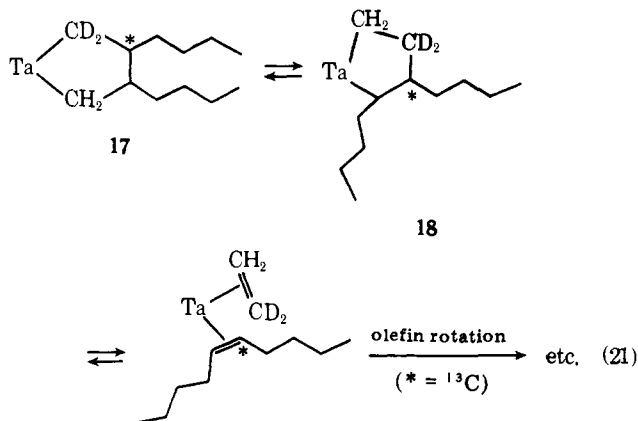
them (eq 21). This would now seem rather unlikely since the above experiment failed and since the necessary metallacycle (**18**) in this case is a type we have not yet seen; it must be of relatively high energy compared to the β,β'-disubstituted isomer.

Experimental Section

All operations were done under N₂, either in Vacuum Atmospheres HE43 glovebox or by Schlenk techniques. Ether and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was purified by an acid wash to remove olefin impurities [3 L of pentane was shaken successively with three 50-mL portions of concentrated H₂SO₄/HNO₃ (95/5) and three 500-mL portions of distilled water followed by drying over CaCl₂], distilled from NaH under nitrogen, and stored over Linde 4 Å molecular sieves until use. Benzene was dried by distilling off the H₂O azeotrope and stored over Linde 4 Å molecular sieves. Styrene (inhibited) was stirred over CaH₂ for 24 h and distilled by a room temperature bulb to bulb transfer in vacuo. Ethylene and propylene (CP grade) were used as received. Mesitylene, olefins, and *n*-alkanes were degassed with nitrogen and passed through a column of activated alumina. Zn(CH₂CH₃)₂ was purchased from Alfa and used as received. TaCp(CHCMe₃)Cl₂,[18] TaCp''(CH₂CMe₃)Cl₃,[18] NbCp(CHCMe₃)Cl₂,[18] Nb(η⁵-C₅H₄Me)-(CHCMe₃)Cl₂,[18] Ta(CH₂CMe₃)₂Cl₃,[36] LiC₅Me₅,[37] TaMe₃Cl₂,[25] C₆H₅CH=CD₂,[38] Tl(C₅H₄Me),[39] and CH₃CH₂CH₂CH₂-CH=CD₂[21,40] were prepared by published methods. Elemental analyses were done by Alfred P. Bernhardt or Schwarzkopf. Chloride analyses were usually done in these laboratories. Samples were digested with 1 M KOH (5 equiv OH⁻/Cl⁻) at 80 °C for 24 h, filtered, and titrated with AgNO₃[41] or Hg(NO₃)₂.[42] ¹H NMR spectra were recorded at 60 and 90 (Perkin-Elmer) or 270 MHz (Bruker) and ¹³C spectra at 15 (JEOL), 22.63 (Bruker), or 67.89 MHz (Bruker). When not specified otherwise, the spectra were recorded at the lowest field strength. GLC yields of organic products are based on the internal standard method using saturated hydrocarbons as standards and a HP 3380A integrator/recorder. Reactions with ethylene and propylene were done in glass pressure bottles connected to a metal head by an O-ring seal.

1. Preparation of CpCl₂TaCH₂CH₂CH₂CH₂. A suspension of red TaCp(CHCMe₃)Cl₂ (2.00 g, 5.17 mmol) in 20 mL of pentane was stirred under 40 psi of ethylene in a glass pressure bottle for 1 h. The color of the solution changed from red to orange as a finely divided, orange, crystalline solid precipitated. The mixture was filtered and the solid was rinsed with pentane (in which it is only slightly soluble) and dried in vacuo, yield 1.67 g (87%). Spectra were recorded under 1 atm of ethylene.

Anal. Calcd for TaC₉H₁₃Cl₂: C, 28.98; H, 3.51; Cl, 19.01. Found: C, 29.03; H, 3.63; Cl, 19.17. ¹H NMR (*τ*, toluene-*d₈*, 32 °C): 4.45 (s, 5, Cp), 7.25 and 7.64 (br singlets, 8, TaCH₂CH₂CH₂CH₂). ¹H NMR (*τ*, toluene-*d₈*, −40 °C): 4.60 (s, Cp), 4.75 (s, dissolved

C₂H₄), 6.35, 7.15, 7.95, and 8.10 (broad singlets TaCH₂CH₂CH₂CH₂). ¹³C NMR (ppm from Me₄Si, C₆D₆, gated decoupled): 112.8 (d, *J*_CH = 181 Hz, Cp), 89.7 (t, *J*_CH = 123 Hz, C_α), 33.5 (t, *J*_CH = 126 Hz, C_β).

The Δ*G*⁺ of pseudorotation was calculated from ¹H NMR spectra measured at intermediate temperatures. The peaks at 6.35 and 7.95 ppm coalesce to give the peak at 7.25 ppm; *δν* = 96 ± 10 Hz and *T*_c = 273 ± 15 K or Δ*G*⁺ = 13.0 ± 0.8 kcal mol⁻¹. The peaks at 7.15 and 8.10 ppm coalesce to give the peak at 7.64 ppm, *δν* = 57 ± 10 Hz and *T*_c = 258 ± 15 K or Δ*G*⁺ = 12.6 ± 0.8 kcal mol⁻¹.

The organic products from the reaction of TaCp(CHCMe₃)Cl₂ with ethylene (40 psi) in mesitylene were analyzed by GLC after passing a sample of the reaction mixture through alumina. The products were 4,4-dimethyl-1-pentene (91 ± 3%) and 4,4-dimethyl-*trans*-2-pentene (3.2 ± 0.4%). No 4,4-dimethyl-*cis*-2-pentene or 3,3-dimethyl-1-butene was detected (<0.1%). All products were identified by GLC comparison with authentic samples on a single column. The major product was also identified by ¹H and ¹³C NMR comparison with authentic samples.

2. Preparation of CpCl₂TaCH₂CHMeCHMeCH₂. TaCp-(CHCMe₃)Cl₂ (2.00 g, 5.17 mmol) was dissolved in a minimal amount of pentane/ether (3/2) and the solution (∼15 mL) was transferred to a glass pressure bottle. The homogeneous red solution was cooled to 0 °C and stirred under 15 psi of propylene for 10 h. At the end of this time an orange solid had formed and the solution was orange; GLC analysis of the solution for 2,4,4-trimethyl-1-pentene vs. an internal standard indicated that the reaction was complete. The pressure in the bottle was reduced to 1 atm and the mixture was cooled to −78 °C for 30 min under a nitrogen atmosphere. The light orange supernatant solution was removed by cannula and the orange solid was washed with 3 × 4 mL of pentane at −78 °C. The pentane washes were each removed by cannula and the solid was warmed to 0 °C and dried in vacuo for 30 min, 1.44 g (70%). NMR samples were prepared and recorded at ≤10 °C to prevent thermal decomposition. The solid can be handled for short periods (∼15 min) at room temperature without significant decomposition.

¹H NMR (*τ*, C₆D₆, 90 MHz, 4 °C): 4.43 (s, 5, Cp), 7.00–9.44 with peaks at 7.43, 7.76, 8.99, and 9.06 (m, 12, TaCH₂CHMeCH-MeCH₂). ¹³C NMR (ppm downfield from Me₄Si, toluene-*d₈*, ¹H decoupled, 7 °C): 24.7 (TaCH₂CHMeCHMeCH₂), 49.7 (TaCH₂CHMeCHMeCH₂), 95.6 (TaCH₂CHMeCHMeCH₂), 113.5 (Cp). See Table I for the low-temperature limiting spectrum.

The Δ*G*⁺ of pseudorotation was calculated from ¹³C NMR spectra measured at intermediate temperatures (67.89 MHz). For C_γ and C_γ', *δν* = 246 ± 20 Hz and *T*_c = 258 ± 10 K or Δ*G*⁺ = 11.8 ± 0.5 kcal mol⁻¹. For C_β and C_β', *δν* = 195 ± 15 Hz and *T*_c = 258 ± 10 K or Δ*G*⁺ = 11.9 ± 0.5 kcal mol⁻¹.

The organic products from the reaction of TaCp(CHCMe₃)Cl₂ with propylene (50 psi) in mesitylene (18 h) were analyzed by GLC after passing a sample of the reaction mixture through alumina. The products were 2,4,4-trimethyl-1-pentene (86 ± 6%) and 2,4,4-trimethyl-2-pentene (3 ± 1%). The major product was identified by coinjection with an authentic sample on two different columns and ¹H and ¹³C NMR comparison to an authentic sample. The minor product was identified by GLC comparison with an authentic sample on one column. Analysis on two additional columns showed the absence of 3,3-dimethyl-1-butene (≤0.4%), 4,4-dimethyl-*trans*-2-pentene (≤0.2%), 2,2-dimethyl-*trans*-3-hexene (≤0.06%), and 2,2-dimethyl-*cis*-3-hexene (∼0%).

3. Preparation of Ta(η⁵-C₅H₄Me)(CHCMe₃)Cl₂. Solid Tl(C₅H₄Me) (3.88 g, 13.69 mmol) was slowly added to a solution of Ta(CH₂CMe₃)₂Cl₃ (5.88 g, 13.69 mmol) in 100 mL of toluene. The solution was stirred for 12 h and filtered to remove TlCl. The toluene was removed in vacuo to give a dark red, crystalline solid which was recrystallized from pentane/toluene (85/15) to give 3.84 g of red needles (70%).

¹H NMR (*τ*, CDCl₃): 3.60 (t, 2, C₅*H₂*^A*H₂*^B Me, *J* = 3 Hz), 3.80 (s, 1, C*H*CMe₃), 4.00 (t, 2, C₅H₂^A*H₂*^B Me, *J* = 3 Hz), 7.78 (s, 3, C₅H₂^A*H₂*^B*Me*), 8.83 (s, 9, CHC*Me₃*). IR (cm⁻¹, Nujol mull): 3110 (w, *ν*_CH, C₅H₄Me), 2528 (w, *ν*_CH. CHC*Me₃*) (cf. TaCp(CHCMe₃)-Cl₂[18]).

4. Preparation of (η⁵-C₅H₄Me)Cl₂TaCH₂CHMeCHMeCH₂. The reaction of Ta(η⁵-C₅H₄Me)(CHCMe₃)Cl₂ (0.70 g, 1.75 mmol) with propylene by the procedure used to prepare CpCl₂TaCH₂CHMeCHMeCH₂ (see above) produced 0.34 g of orange solid, (η⁵-C₅H₄Me)Cl₂TaCH₂CHMeCHMeCH₂ (47%). The

solid darkens rapidly at room temperature and becomes sticky. NMR samples were prepared and recorded at ≤0 °C.

^{1}H NMR (τ, toluene-d_8, 270 MHz, -10 °C): 4.18 (br s, 1, $C_5H_AH_BH_CH_DMe$), 4.24 (br s, 1, $C_5H_AH_BH_CH_DMe$), 4.61 (br s, 1, $C_5H_AH_BH_CH_DMe$), 4.74 (br s, 1, $C_5H_AH_BH_CH_DMe$), 6.93–9.29 (m, 6, TaCH_2CHMeCHMeCH_2), 8.19 (s, 3, C_5H_4Me), 9.02 (s, 3, TaCH$_2$CHMeCHMeCH$_2$), 9.05 (s, 3, TaCH$_2$CHMeCHMeCH$_2$).

5. Reaction of TaCp(CHCMe₃)Cl₂ with Styrene. TaCp-(CHCMe₃)Cl₂ (0.39 g, 1.0 mmol) and styrene (0.31 g, 3.0 mmol) were combined in 3 mL of benzene. The solution became darker within 10 min and after 2 h a dark precipitate had formed. The solution was filtered to yield a dark brown solid. This solid was slightly soluble in C_6D_6 and moderately soluble in CD_2Cl_2 but neither solution gave an NMR signal. The dark solid was not characterized further.

TaCp(CHCMe₃)Cl₂ (0.39 g, 1.0 mmol) and styrene (0.10 g, 1.0 mmol) were stirred for 12 h in 0.5 mL of C_6D_6. The volatile products were isolated by a bulb to bulb transfer in vacuo at ~60 °C. GLC analysis on two different columns showed a single major high-boiling product which accounted for >90% of the product mixture. It was identified as *trans*-C_6H_5CH=CHCH₂CMe₃ by comparison of its ^{1}H NMR and IR spectra with those for authentic samples of *cis*- and *trans*-C_6H_5CH=CHCH₃. ^{1}H NMR (τ, C_6D_6): 2.88 (m, C_6H_5), 3.75 (m, 2, C_6H_5CH=CHCH₂CMe₃), 8.02 (d, 2, $^3J_{HH}$ = 6 Hz, C_6H_5CH=CHCH_2CMe₃), 9.10 (s, 9, CMe₃). ^{13}C NMR (ppm downfield of Me₄Si, C_6D_6, ^{1}H decoupled): 29.6 (CMe_3), 31.4 (CMe_3), 47.9 (CH₂), 127.2, 128.8, 132.7 (the remaining peaks overlap with C_6D_6). IR (C_6D_6, solution cells): 970 cm^{-1} (CH out-of-plane bend).

The total yield of *tert*-butyl-containing products (95 ± 10%) was determined for the reaction of TaCp(CHCMe₃)Cl₂ with 3 equiv of styrene by passing the reaction mixture through alumina and integrating the CMe₃ protons vs. cyclohexane internal standard.

6. Reaction of NbCp(CHCMe₃)Cl₂ with Ethylene. NbCp-(CHCMe₃)Cl₂ (0.028 g, 0.094 mmol) was dissolved in 5 mL of mesitylene and stirred under ethylene (50 psi) for 1 h. A sample of the dark solution was passed through alumina and the products were identified by GLC comparison with authentic samples on a single column: 4,4-dimethyl-1-pentene (62 ± 3%), 4,4-dimethyl-*trans*-2-pentene (2%). Less than 0.1% 4,4-dimethyl-*cis*-2-pentene or 3,3-dimethyl-1-butene was present.

7. Reaction of NbCp(CHCMe₃)Cl₂ with Propylene. NbCp-(CHCMe₃)Cl₂ (0.0641 g, 0.214 mmol) was dissolved in 10 mL of decane and stirred under propylene (40 psi) at 45 °C for 12 h. The purple solution gradually became colorless as a dark precipitate formed. A sample of the mixture was shaken with air and the organic products were identified by GLC comparison with authentic samples on a single column: 2,4,4-trimethyl-1-pentene (55%), 2,4,4-trimethyl-2-pentene (7%).

8. Reaction of Nb(η^5-C_5H_4Me)(CHCMe₃)Cl₂ with Ethylene. A solution of 0.236 g of Nb(η^5-C_5H_4Me)(CHCMe₃)Cl₂ in 20 mL of pentane was stirred for 1 h under 40 psi of ethylene. The brown precipitate was filtered off and the almost colorless pentane filtrate analyzed for 4,4-dimethyl-1-pentene (87%).

9. Preparation of TaCp″Me₃Cl. Solid LiC₅Me₅ (2.91 g, 20.4 mmol) was added to a solution of TaMe₃Cl₂ (6.07 g, 20.4 mmol) in 80 mL of ether with vigorous stirring. The mixture was stirred for 2 h and filtered. The ether was removed in vacuo and the yellow, crystalline solid was extracted into a minimal amount of toluene and filtered. Toluene was removed in vacuo until crystals began to form at which time two volumes of pentane were added and the solution was cooled to -30 °C for 12 h. The yellow crystals were filtered and dried in vacuo, yield 5.37 g. A second crop was obtained by removing the solvent from the filtrate in vacuo and recrystallizing the residue from pentane/toluene (3/1) at -30 °C, yield 1.01 g (overall 78%).

^{1}H NMR (τ, C_6H_6): 8.25 (s, 15, C_5Me_5), 9.10 (s, 9, Me). ^{1}H NMR (τ, toluene-d_8, -40 °C, 270 MHz): 8.38 (s, C_5Me_5), 9.12 (s, 3, Me), 9.14 (s, 6, Me′). ^{13}C NMR (ppm downfield from Me₄Si, toluene-d_8, ^{1}H decoupled): 11.6 (C_5Me_5), 72.8 (Me), 120.5 (C_5Me_5). ^{13}C NMR (ppm downfield from Me₄Si, toluene-d_8, -78 °C, ^{1}H decoupled): 11.6 (C_5Me_5), 71.5 (Me), 73.1 (Me′), 120.0 (C_5Me_5).

An approximate value for $\Delta G^\ddagger$ of pseudorotation can be estimated by assuming an equal population two-site exchange. ^{1}H NMR spectra recorded at intermediate temperatures were used for this calculation (270 MHz). For Me and Me′, $\delta\nu$ = 8 ± 4 Hz and T_c = 258 ± 20 K or $\Delta G^\ddagger$ = 13.6 ± 1.4 kcal mol^{-1}.

10. Preparation of TaCp″(C_2H_4)Cl₂. TaCp″(CH₂CMe₃)Cl₃ (4.94

g, 10.0 mmol) was dissolved in 60 mL of toluene and cooled to -78 °C. A solution of Zn(CH₂CH₃)₂ (0.77 g, 6.25 mmol) in 10 mL of toluene was added dropwise to the cold solution. At the end of the addition the mixture was allowed to warm slowly to room temperature. The color changed from dark orange to red-purple. The solution was filtered and the toluene was removed from the filtrate in vacuo. The resulting dark solid was recrystallized from ether at -30 °C to give dark purple crystals (1.69 g). A second crop was recrystallized from pentane/toluene (80/20) to give an additional 0.36 g (overall yield 50%).

Anal. Calcd for TaC₁₂H₁₉Cl₂: C, 34.72; H, 4.61; Cl, 17.08. Found: C, 35.03; H, 4.70; Cl, 17.02. ^{1}H NMR (τ, C_6H_6): 7.62 (s, 4, C_2H_4), 8.37 (s, 15, C_5Me_5). ^{1}H NMR (τ, toluene-d_8, -100 °C, 270 MHz): 7.32 (br s, H_AH_BC=CH_BH_A), 7.93 (br s, H_AH_BC=CH_BH_A), 8.57 (s, C_5Me_5). ^{13}C NMR (ppm downfield from Me₄Si, C_6D_6, 67.89 MHz, ^{1}H gated decoupled): 11.6 (q, C_5Me_5, $^1J_{CH}$ = 129 Hz), 69.4 (t, C_2H_4, $^1J_{CH}$ = 151 Hz), 117.3 (s, C_5Me_5).

The $\Delta G^\ddagger$ of olefin rotation was calculated from ^{1}H NMR spectra measured at intermediate temperatures (270 MHz). For H_A and H_B, $\delta\nu$ = 166 ± 20 Hz and T_c = 203 ± 5 K or $\Delta G^\ddagger$ = 9.3 ± 0.3 kcal mol^{-1}.

11. Preparation of ZnCl₂(dioxane).[43] ZnCl₂ (200 g, 1.47 mol) was added to a 2-L flask equipped with a side arm attached to a nitrogen line. Ether (1.5 L) was added and the mixture was stirred for 3 h under N₂. Most of the ZnCl₂ dissolved. The solution was Schlenk filtered into a 3-L flask equipped with a N₂ inlet and septum inlet. Dioxane (129.3 g, 1.47 mol) was added by syringe to the stirred solution. An immediate reaction yielded a white precipitate. At the end of the addition the mixture was stirred for 1 h and filtered through a large Schlenk filter. The white solid was dried in vacuo for 12 h to give 261.1 g (79%) of hygroscopic ZnCl₂(dioxane). It was stored and transferred under nitrogen.

12. Preparation of Zn(CH₂CH₂CH₃)₂. A Grignard reagent was prepared from 14.59 g of Mg (0.6 mol) and 61.5 g of *n*-propyl bromide (0.5 mol) in 300 mL of ether in a 1-L three-neck flask and stirred for 8 h at 25 °C. The mixture was cooled to 0 °C and ZnCl₂(dioxane) (61.7 g, 0.275 mol) was added over a period of 1 h from a 250-mL flask connected to the reaction flask with a plastic tube. The mixture was stirred for 12 h at 25 °C and filtered inside a drybox. The white precipitate was washed with 3 × 300 mL of ether and the combined filtrates were concentrated in vacuo. Distillation in a spinning band column at 10 mm (39–41 °C) gave 27.71 g (73%) of colorless Zn(CH₂CH₂CH₃)₂. ^{1}H NMR (τ, C_6H_6): 8.48 (m, ZnCH₂CH_2CH₃), 9.00 (t, J_{CH} = 7 Hz, ZnCH₂CH₂CH_3), 9.70 (t, J_{CH} = 7Hz, ZnCH_2CH₂CH₃).

13. Preparation and Thermal Decomposition of TaCp″(propylene)Cl₂. A solution of Zn(CH₂CH₂CH₃)₂ (1.86 g, 12.29 mmol) in 10 mL of toluene was rapidly added to a solution of TaCp″-(CH₂CMe₃)Cl₃ (9.71 g, 19.61 mmol) in 140 mL of toluene at -78 °C. After stirring for 5 min at -78 °C the cold bath was removed and the stirred solution was allowed to warm to room temperature. The color changed from orange to purple-red and a dark solid precipitated. The mixture was filtered and the precipitate was extracted with toluene until the filtrate was colorless. The toluene was removed in vacuo from the combined filtrates to give a dark solid which was recrystallized from pentane at -30 °C to give 6.39 g of dark purple crystals (two crops, 76% total yield).

Anal. Calcd for TaC₁₃H₂₁Cl₂: C, 36.39; H, 4.93; Cl, 16.52. Found: C, 36.58; H, 5.06; Cl, 16.66. ^{1}H NMR (τ, C_6H_6): 6.98–8.20 including a large peak at 7.12 (m, 6, CH₃CH=CH₂), 8.37 (s, 15, C_5Me_5). ^{13}C NMR (ppm downfield from Me₄Si, toluene-d_8, 0 °C, ^{1}H gated decoupled): 11.6 (q, C_5Me_5, J_{CH} = 128 Hz), 27.3 (q, CH₃CH=CH₂, $^1J_{CH}$ = 125 Hz), 72.3 (t, CH₃CH=CH₂, $^1J_{CH}$ = 149 Hz), 80.0 (d, CH₃CH=CH₂, $^1J_{CH}$ = 152 Hz), 117.2 (s, C_5Me_5).

A 0.43-g (1.00 mmol) sample of TaCp″(propylene)Cl₂ was dissolved in 10 mL of C_6H_5Cl and heated to 100 °C for 45 min. An ^{1}H NMR spectrum of the dark orange solution showed peaks due to 2,3-dimethyl-1-butene but also many unidentifiable ones. The solution was filtered to give 0.16 g of sparingly soluble, dark green crystals which analyzed as TaCp″Cl₃. (Anal. Calcd for TaC₁₀H₁₅Cl₃: C, 28.42; H, 3.58; Cl, 25.17. Found: C, 28.88; H, 4.10; Cl, 25.59.) The compound was too insoluble in nonreacting solvents for NMR spectroscopy but was characterized further by preparation of the soluble PMe₃ adduct (see preparation 33).

14. Preparation of TaCp″(styrene)Cl₂. (a) From TaCp″(C_2H_4)Cl₂. A solution of TaCp″(C_2H_4)Cl₂ (0.42 g, 1.00 mmol) in 2 mL of C_6H_6

was added to a solution of styrene (0.23 g, 2.20 mmol) in 3 mL of C_6H_6. An ^1H NMR spectrum recorded after 15 min showed a 1:1 mixture of $Cp''Cl_2\overline{Ta}CH_2CH_2CH_2CH_2$ and $TaCp''(styrene)Cl_2$ along with excess free styrene. After 1 h at 25 °C the ^1H NMR spectrum showed no further change. The mixture was heated at 70 °C for 1 h and the ^1H NMR spectrum showed almost complete conversion to $TaCp''(styrene)Cl_2$. The solvent was removed in vacuo and the solid was recrystallized from toluene/pentane (50/50) at −30 °C to give 0.27 g (54%) of dark purple crystals. A GLC analysis suggested that there were no styrene/ethylene codimers in the final reaction mixture.

(b) From TaCp''(propylene)Cl₂. $TaCp''(propylene)Cl_2$ (0.86 g, 2.0 mmol) and styrene (0.62 g, 6.0 mmol) were stirred in 10 mL of benzene for 24 h. The benzene was·removed in vacuo and the dark solid was extracted into pentane/toluene (50/50) and filtered. Cooling the filtrate to −30 °C for 12 h produced 0.69 g of dark purple crystals. The filtrate was concentrated to a solid in vacuo and recrystallized from pentane/toluene (75/25) at −30 °C to give an additional 0.07 g, overall yield 77%. The only organic product observed in ^1H NMR spectra of the reaction mixture was 2,3-dimethyl-1-butene.

^1H NMR (τ, C_6H_6, 90 MHz): 6.56 (t, 1, C_6H_6CH=CH_2, $^3J_{HH}$ = 12 Hz), 7.00-7.90 (m, 2, C_6H_5CH=CH_2), 8.33 (s, 15, C_5Me_5). ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, ^1H decoupled): 11.8 (C_5Me_5), 67.7 (C_6H_5CH=CH_2), 85.2 (C_6H_5CH=CH_2), 118.5 (C_5Me_5), 125.1 126.1, 127.3, 149.9 (C_6H_5CH=CH_2).

15. Preparation of TaCp''(1-pentene)Cl₂. $TaCp''(propylene)Cl_2$ (3.43 g, 8.0 mmol) and 1-pentene (2.81 g, 40.0 mmol) were combined in 25 mL of toluene. After stirring for 5 min the color of the solution changed from red-purple (Ta(III) olefin complex) to orange (Ta(V) metallacycle). The color changed back to red-purple within 12 h and after 24 h the toluene was removed in vacuo to give a dark solid. Recrystallization of the crude product from pentane at −30 °C yielded 3.16 g of dark purple crystals (two crops, 86% total yield).

^1H NMR (τ, C_6H_6): 7.00-9.20 including peaks at 7.33 (m), 8.90 (br s), 9.02 (s), and 9.13 (s) (m, 1-pentene), 8.37 (s, C_5Me_5). ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, ^1H gated decoupled): 11.8 (q, C_5Me_5, $^1J_{CH}$ = 129 Hz), 14.4 (q, CH_2=$CHCH_2CH_2CH_3$, $^1J_{CH}$ = 125 Hz), 29.0, 43.3 (t, t, CH_2=$CHCH_2CH_2CH_3$, $^1J_{CH}$ = 125, 126 Hz), 72.9 (t, CH_2=$CHCH_2CH_2CH_3$, $^1J_{CH}$ = 142 Hz), 87.0 (d, CH_2=$CHCH_2CH_2CH_3$, $^1J_{CH}$ = 152 Hz), 117.6 (s, C_5Me_5).

$TaCp''(propylene)Cl_2$ (0.1491 g, 0.3474 mmol) was added to a 9-mm tube connected to a ball joint. Mesitylene (0.5 mL), *n*-heptane (20 μL, 0.135 mmol), and 1-pentene (190 μL, 1.74 mmol) were added by syringe and the tube was connected to a vacuum line. The solution was frozen in liquid N_2 and the tube was sealed off under ~500 mm N_2. After 48 h the tube was cooled and opened. A sample of the solution was transferred by syringe to a septum-capped vial containing dry O_2. GC/mass spectral analysis showed pentenes, 2,3-dimethyl-1-butene (0.10 equiv/Ta), *n*-heptane internal standard, two peaks of formula C_8H_{16} (0.84 equiv/Ta), and two dimers of 1-pentene. The parent ion of each product was detected and there were no significant higher mass peaks. The presence of 2,3-dimethyl-1-butene was confirmed by comparison to a GC/mass spectrum of an authentic sample. The relative response of the C_8H_{16} products vs. *n*-heptane standard was assumed to be the ratio of their molecular weights.

16. Preparation of TaCp''(cis-2-pentene)Cl₂. $TaCp''(propylene)Cl_2$ (0.64 g, 1.5 mmol) and *cis*-2-pentene (0.32 g, 4.5 mmol) were stirred in 15 mL of benzene for 24 h. The benzene was removed in vacuo and the dark solid was recrystallized from a minimal amount of pentane at −30 °C to give 0.51 g of dark purple crystals (two crops, 74% total yield).

Anal. Calcd for $TaC_{15}H_{25}Cl_2$: C, 36.39; H, 4.93; Cl, 15.51. Found: C, 36.58; H, 5.06; Cl, 15.77. ^1H NMR (τ, C_6D_6, 90 MHz): 6.30-7.97 including large peaks at 7.13 and 7.19 (m, 7, CH_3CH=CH-CH_2CH_3), 8.27 (s, 15, C_5Me_5), 9.01 (t, 3, CH_3CH=$CHCH_2CH_3$, $^3J_{HH}$ = 7 Hz). ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, ^1H gated decoupled): 11.8 (q, C_5Me_5, $^1J_{CH}$ = 128 Hz), 18.9, 19.2 (q, q, CH_3CH=$CHCH_2CH_3$, $^1J_{CH}$ = 124 Hz), 27.7 (t, CH_3CH=$CHCH_2CH_3$, $^1J_{CH}$ = 127 Hz), 80.2, 87.3 (d, d, CH_3CH=$CHCH_2CH_3$, $^1J_{CH}$ = 152, 148 Hz), 117.9 (s, C_5Me_5).

$TaCp''(propylene)Cl_2$ (0.1288 g, 0.300 mmol) was placed in a septum-capped 9-mm tube. Mesitylene (0.5 mL), *n*-heptane internal standard (20 μL, 0.135 mmol), and *cis*-2-pentene (161 μL, 1.50 mmol) were added by syringe. The mixture was frozen in liquid N_2 and the tube was sealed off under 1 atm of N_2. After 36 h the tube was cooled and opened. A sample of the solution was transferred by syringe

to a septum-capped vial containing dry O_2. GC/mass spectral analysis showed *cis*-2-pentene, 2,3-dimethyl-1-butene (0.44 equiv/Ta), *n*-heptane internal standard, and two products of formula C_8H_{16} (0.06 equiv/Ta). The parent ion of each product was detected and there were no significant higher mass peaks. The presence of 2,3-dimethyl-1-butene was confirmed by comparison to a GC/mass spectrum of an authentic sample. The relative response of the C_8H_{10} products vs. *n*-heptane standard was assumed to be the ratio of their molecular weights.

17. Preparation of TaCp''(cyclooctene)Cl₂. $TaCp''(propylene)Cl_2$ (0.43 g, 1.00 mmol) and cyclooctene (0.33 g, 3.00 mmol) were combined in 6 mL of benzene. After 12 h at 25 °C the benzene was removed in vacuo. The dark residue was recrystallized from toluene at −30 °C to produce 0.16 g of dark purple crystals. The solvent was removed from the filtrate in vacuo and the solid was recrystallized from pentane/toluene (80/20) to give a second crop of 0.18 g (overall yield 68%). The only organic product observed in ^1H NMR spectra of the reaction mixture was 2,3-dimethyl-1-butene.

^1H NMR (τ, C_6D_6): 6.90-9.20 with a broad singlet at 7.33 (m, cyclooctene), 8.39 (s, C_5Me_5). ^{13}C NMR (ppm downfield of Me_4Si, toluene-d_8, ^1H decoupled): 11.6 (C_5Me_5), 17.9, 26.9, 33.8, 39.4 (aliphatic cyclooctene carbon atoms), 86.0 (olefinic cyclooctene carbon atoms), 117.6 (C_5Me_5).

18. Preparation of TaCp''(neopentylethylene)Cl₂. $TaCp''(propylene)Cl_2$ (0.43 g, 1.0 mmol) and 4,4-dimethyl-1-pentene (0.35 g, 5.0 mmol) were stirred in 10 mL of toluene for 24 h. The toluene was removed in vacuo and the dark gummy solid was recrystallized from a minimal amount of pentane at −30 °C to give 0.38 g of dark purple crystals (78%).

^1H NMR (τ, C_6D_6): 6.80-8.50 (m, 5, Me_3CCH_2CH=CH_2), 8.25 (s, 15, C_5Me_5), 9.05 (s, 9, Me_3CCH_2CH=CH_2). ^{13}C NMR (ppm downfield from Me_4Si, C_6D_6, ^1H gated decoupled): 11.6 (q, C_5Me_5, $^1J_{CH}$ = 128 Hz), 29.7 (q, Me_3CCH_2CH=CH_2, $^1J_{CH}$ = 124 Hz), 38.1 (s, Me_3CCH_2CH=CH_2), 55.1 (t, Me_3CCH_2CH=CH_2, $^1J_{CH}$ = 126 Hz), 75.5 (t, Me_3CCH_2CH=CH_2, $^1J_{CH}$ = 150 Hz), 81.6 (d, Me_3CCH_2CH=CH_2, $^1J_{CH}$ = 150 Hz), 117.4 (s, C_5Me_5).

$TaCp''(propylene)Cl_2$ (0.1499 g, 0.349 mmol) was placed in a septum-capped 9-mm tube. Mesitylene (0.5 mL), *n*-heptane internal standard (20 μL, 0.135 mmol), and 4,4-dimethyl-1-pentene (251 μL, 1.75 mmol) were added by syringe. The mixture was frozen in liquid N_2 and the tube was sealed off under 1 atm of N_2. After 36 h the tube was cooled and opened. A sample of the solution was transferred by syringe to a septum-capped vial containing dry O_2. GC/mass spectral analysis showed 4,4-dimethyl-1-pentene, 2,3-dimethyl-1-butene (0.34 equiv/Ta), *n*-heptane internal standard, two products of formula $C_{10}H_{20}$ (0.39 equiv/Ta), and a dimer of 4,4-dimethyl-1-pentene ($C_{14}H_{28}$). The parent ion of each product was detected and there were no significant higher mass peaks. The presence of 2,3-dimethyl-1-butene was confirmed by comparison of its GC/mass spectrum with that of an authentic sample. The relative response of the $C_{10}H_{20}$ products vs. *n*-heptane was assumed to be the ratio of their molecular weights.

19. Reaction of TaCp''(propylene)Cl₂ with *trans*-2-pentene. $TaCp''(propylene)Cl_2$ (0.43 g, 1.00 mmol) and *trans*-2-pentene (0.18 g, 2.6 mmol) were combined in 5 mL of benzene. ^1H NMR spectra of the reaction mixture were very complex and included two sharp peaks at τ 8.25 and 8.35 which are probably the C_5Me_5 resonances of a metallacyclopentane complex and an olefin complex, respectively. After 25 h the resonance at τ 8.25 had disappeared and a new olefinic resonance had appeared at τ 5.25; no $TaCp''(propylene)Cl_2$ remained. The solvent was removed in vacuo and the dark solid was extracted with pentane. The green-brown pentane-insoluble portion (0.11 g) was soluble in benzene but gave only weak signals in the ^1H NMR spectrum. The pentane-soluble portion was recrystallized from pentane at −30 °C to give 0.10 g of a dark, crystalline solid which was identified as ≥85% $TaCp''(1-pentene)Cl_2$ by ^1H and ^{13}C NMR.

20. Reaction of TaCp''(propylene)Cl₂ with Isobutylene. A fivefold excess of isobutylene was added to an NMR sample of $TaCp''(propylene)Cl_2$ (60 mg). There was no immediate reaction, but after 24 h there were peaks due to 2,3-dimethyl-1-butene and new sharp peaks at τ 7.15 and 8.27, in addition to starting material. The ^1H NMR spectrum did not change further during the next 3 days. The solvent was removed in vacuo and a ^{13}C NMR spectrum of the residue was recorded; the only compound observed was $TaCp''(propylene)Cl_2$.

A 60-mg sample of $TaCp''(propylene)Cl_2$ was dissolved in C_6H_6 and the solution was stirred under 10 psi of isobutylene at 50 °C for

30 min. The solution changed from dark red to dark orange and a precipitate formed. The solvent was removed in vacuo. An ^{1}H NMR spectrum of the residue showed a broad doublet at τ 7.9. No starting material remained and there was no evidence for formation of TaCp″(isobutylene)Cl$_2$.

21. Attempted Preparation of TaCp(C$_2$H$_4$)Cl$_2$. TaCp(CH$_2$CMe$_3$)-Cl$_3$ (0.42 g, 1.00 mmol) was dissolved in 8 mL of toluene and cooled to −78 °C to give a homogeneous orange solution. Zn(CH$_2$CH$_3$)$_2$ (0.077 g, 0.63 mmol) dissolved in 2 mL of toluene was added dropwise over a period of 15 min. There was an immediate reaction to give initially a darker solution, then an orange precipitate. The mixture was gradually warmed to 25 °C and the solvent was removed in vacuo. The orange residue was extracted with toluene (5 mL). The mixture was filtered and the toluene was removed from the filtrate, leaving 70 mg of a dark orange solid whose ^{1}H NMR spectrum in C$_6$D$_6$ was complex and uninterpretable. The toluene-insoluble fraction of the product could not be characterized.

22. Preparation of Cp″Cl$_2$TaCH$_2$CH$_2$CH$_2$CH$_2$. A suspension of TaCp″(C$_2$H$_4$)Cl$_2$ (0.50 g, 1.20 mmol) in 12 mL of pentane was stirred under 40 psi of ethylene in a glass pressure bottle. Over a period of 15 min the dark suspended solid disappeared and an orange, crystalline solid precipitated. The mixture was filtered and the orange solid was rinsed with pentane and dried in vacuo, yield 0.43 g (81%). Samples for analysis were recrystallized at −30 °C from methylcyclohexane or pentane/toluene (75/25). NMR spectra were recorded under 1 atm of ethylene.

Anal. Calcd for TaC$_{14}$H$_{23}$Cl$_2$: C, 37.94; H, 5.23; Cl, 16.00. Found: C, 37.63; H, 5.35; Cl, 16.32. ^{1}H NMR (τ, C$_6$H$_6$): 6.85 (m, 4, TaCH$_2$CH$_2$CH$_2$CH$_2$), 8.20 (s, 15, C$_5$Me$_5$), 8.70 (m, 4, TaCH$_2$CH$_2$CH$_2$CH$_2$). ^{1}H NMR (τ, toluene-d_8, −60 °C, 270 MHz): 6.66 (br s, H$_\alpha$), 6.93 (br s, H$_\alpha'$), 8.33 (s, C$_5$Me$_5$), 8.78 (br s, H$_\beta$), 8.90 (br s, H$_\beta'$). $\Delta G^\ddagger$ for pseudorotation was calculated from ^{1}H NMR spectra at intermediate temperatures (270 MHz). For H$_\alpha$ and H$_\alpha'$, $\delta\nu$ = 73 ± 8 Hz and T_c = 270 ± 7 K or $\Delta G^\ddagger$ = 13.0 ± 0.4 kcal mol^{-1}. For H$_\beta$ and H$_\beta'$, $\delta\nu$ = 32 ± 10 Hz and T_c = 253 ± 10 K or $\Delta G^\ddagger$ = 12.6 ± 0.7 kcal mol^{-1}.

23. Preparation of Cp″Cl$_2$TaCH$_2$CHMeCHMeCH$_2$. A solution of TaCp″(propylene)Cl$_2$ (0.65 g, 1.51 mmol) in 15 mL of pentane in a glass pressure bottle was stirred under 40 psi of propylene. Within 5 min orange crystals of the metallacycle formed in the solution. The propylene connection was shut off and the mixture was stirred for 1 h at 0 °C. The light orange supernatant solution was removed by syringe and the product was dried in vacuo for 30 min at 0 °C to give 0.56 g (78%). NMR samples were prepared and recorded at ≤10 °C to prevent thermal decomposition. The solid can be handled at room temperature for short periods (~15 min) without significant decomposition.

^{1}H NMR (τ, toluene-d_8, 0 °C): 7.05, 8.55, 8.64, and 9.14 (broad s or m, 12, TaCH$_2$CHMeCHMeCH$_2$), 8.17 (s, 15, C$_5$Me$_5$). ^{13}C NMR (ppm downfield from Me$_4$Si, toluene-d_8, ^{1}H decoupled, 0 °C): 12.1 (C$_5$Me$_5$), 21.0 (TaCH$_2$CHMeCHMeCH$_2$), 82.9 (very broad, TaCH$_2$CHMeCHMeCH$_2$), 122.9 (C$_5$Me$_5$), the peaks for the β-carbon atoms are close to the coalescence point. See Table 1 for the low-temperature limiting ^{13}C NMR spectrum.

The $\Delta G^\ddagger$ for pseudorotation was calculated from ^{13}C NMR spectra measured at intermediate temperatures. For C$_\alpha$ and C$_\alpha'$, $\delta\nu$ = 108 ± 10 Hz and T_c = 251 ± 8 K or $\Delta G^\ddagger$ = 11.9 ± 0.4 kcal mol^{-1}. For C$_\beta$ and C$_\beta'$, $\delta\nu$ = 194 ± 15 Hz and T_c = 258 ± 8 K or $\Delta G^\ddagger$ = 11.9 ± 0.4 kcal mol^{-1}. For C$_\gamma$ and C$_\gamma'$, $\delta\nu$ = 19.5 ± 5 Hz and T_c = 237 ± 15 K or $\Delta G^\ddagger$ = 12.0 ± 0.9 kcal mol^{-1}.

24. Preparation of Cp″Cl$_2$TaCH$_2$CH(n-C$_3$H$_7$)CH(n-C$_3$H$_7$)CH$_2$. TaCp″(1-pentene)Cl$_2$ (0.54 g, 1.18 mmol) was dissolved in a minimal amount of pentane and 1-pentene (0.25 g, 3.54 mmol) was added with stirring. After 3 min the orange metallacycle began to crystallize from solution. Shortly thereafter the solution became too thick to stir. Enough pentane/toluene (80/20) was added to dissolve all of the metallacycle. The solution was filtered and cooled to −30 °C for 12 h to give 0.43 g of orange crystals. The solvent was removed from the filtrate in vacuo and the solid was redissolved in a minimal amount of pentane/toluene (80/20) with a few drops of 1-pentene. This solution was filtered and cooled to −30 °C for 12 h to produce a second crop of 0.04 g (total yield 75%).

^{1}H NMR (τ, toluene-d_8, −40 °C): 6.31 (br m), 6.97–9.81 (complex pattern including broad peak at 8.92), 8.18 (C$_5$Me$_5$). See Table 1 for ^{13}C NMR spectrum.

25. Observation of Cp″Cl$_2$TaCH$_2$CH(CH$_2$CMe$_3$)CH(CH$_2$-CMe$_3$)CH$_2$. TaCp″(Me$_3$CCH$_2$CH=CH$_2$)Cl$_2$ (0.60 g, 1.40 mmol) was dissolved in 1.5 mL of toluene-d_8 and Me$_3$CCH$_2$CH=CH$_2$ (0.55 g, 5.60 mmol) was added. The mixture was cooled to 0 °C and maintained at that temperature for 24 h. A ^{13}C NMR spectrum of the dark orange solution showed Cp″Cl$_2$TaCH$_2$CH(CH$_2$CMe$_3$)-CH(CH$_2$CMe$_3$)CH$_2$ and TaCp″(Me$_3$CCH$_2$CH=CH$_2$)Cl$_2$ in a ratio of 3:1. ^{1}H NMR (τ, toluene-d_8, 0 °C): 8.19 (s, C$_5$Me$_5$), 8.99 (s, CH$_2$C*Me*$_3$). ^{13}C NMR (ppm downfield of Me$_4$Si, toluene-d_8, 67.89 MHz, −40 °C, ^{1}H gated decoupled); 12.7 (q, C$_5$*Me*$_5$, $^1J_{CH}$ = 129 Hz), 30.0, 31.2, 31.5, 32.1, 32.2, 44.4, 48.2, 53.2 (unassigned), 79.1 (t, C$_\alpha$, $^1J_{CH}$ = 127 Hz), 88.4 (t, C$_\alpha'$, $^1J_{CH}$ = 128 Hz), 122.6 (s, C$_5$Me$_5$). The complexity of the ^{1}H gated decoupled spectrum prevented the assignment of most resonances except the crucial C$_\alpha$ and C$_\alpha'$ signals. All chemical shifts were determined from a ^{1}H decoupled spectrum.

26. Reaction of TaCp″(styrene)Cl$_2$ with β,β-Dideuteriostyrene. An ^{1}H NMR spectrum of a 1:1 mixture of TaCp″(styrene)Cl$_2$ and styrene showed no evidence of reaction. Two equivalents of β,β-dideuteriostyrene was added to an NMR sample of TaCp″(styrene)Cl$_2$ in C$_6$D$_6$. The ^{1}H NMR spectrum taken after 15 min showed free styrene-d_0 resonances and a new broad peak at τ 6.60 which was assigned to TaCp″(C$_6$H$_5$C*H*=CD$_2$)Cl$_2$. Eight equivalents more of β,β-dideuteriostyrene was added. The ^{1}H NMR spectrum was then virtually solely that of TaCp″(C$_6$H$_5$CH=CD$_2$)Cl$_2$ [(τ, C$_6$D$_6$): 2.80 (m, C$_6$H$_5$), 6.60 (br s, C$_6$H$_5$C*H*=CD$_2$), 8.35 (s, C$_5$Me$_5$)] and free styrene-d_0 and -d_2.

27. Reaction of TaCp″(C$_2$H$_4$)Cl$_2$ with Styrene. TaCp″(C$_2$H$_4$)Cl$_2$ (0.076 g, 0.18 mmol) was dissolved in a minimal amount of toluene-d_8 (~0.5 mL) and transferred to a septum-capped 5-mm NMR tube. The sample was cooled to −35 °C and styrene (25 μL, 0.22 mmol) was added by syringe. The tube was shaken briefly to mix the reactants. The ^{13}C NMR spectrum recorded immediately at −38 °C showed a 1:1 mixture of TaCp″(styrene)Cl$_2$, Cp″Cl$_2$TaCH$_2$CH$_2$CH$_2$CH$_2$, and free styrene. There was no evidence for the formation of a mixed metallacycle.

28. Preparation and Decomposition of Cp″Cl$_2$TaCH$_2$CH-MeCH$_2$CH$_2$. TaCp″(C$_2$H$_4$)Cl$_2$ (0.18 g, 0.43 mmol) was dissolved in 1.5 mL of toluene-d_8 and the solution was put into a septum-capped 10-mm NMR tube. The solution was cooled to −35 °C and propylene (11.7 mL, 0.52 mmol) was added by syringe over a period of 1 min. The sample was shaken several times during the addition and after 15 min the color had changed from dark red to orange. ^{13}C NMR spectra were recorded at various temperatures. The first spectrum recorded at −35 °C shows only a mixture of two β-substituted metallacyclopentanes (see Table 1). ^{1}H NMR (τ, toluene-d_8, −45 °C): 7.0–9.5 (complex, several peaks, TaCH$_2$CHMeCH$_2$CH$_2$), 8.24 (s, C$_5$Me$_5$). ^{13}C NMR spectra recorded at intermediate temperatures show a fluxional process which interconverts these two isomers. Peak assignments were based on chemical shifts, peak multiplicities in gated decoupled spectra, and how peaks collapse and reappear upon warming the sample. The spectrum of Cp″Cl$_2$TaCH$_2$CHMeCH$_2$CH$_2$ which is closest to the high-temperature limit was recorded at 10 °C and 15.00 MHz. ^{13}C NMR (ppm downfield from Me$_4$Si, toluene-d_8, 10 °C, ^{1}H decoupled): 12.1 (C$_5$*Me*$_5$), 26.6 (TaCH$_2$CHMeCH$_2$CH$_2$), 31.3 (TaCH$_2$CHMeCH$_2$CH$_2$), 122.7 (C$_5$Me$_5$). The remaining ring carbon atom signals are still too broad to be detected at this temperature. After several hours at 10 °C, the ^{13}C NMR spectrum recorded at −40 °C and 67.89 MHz shows Cp″Cl$_2$TaCH$_2$CHMeCHMeCH$_2$, Cp″Cl$_2$TaCH$_2$CHMeCH$_2$CH$_2$, Cp″Cl$_2$TaCH$_2$CH$_2$CH$_2$CH$_2$, and TaCp″(C$_2$H$_4$)Cl$_2$ in the ratio 20:55:20:5. After 30 min at 52 °C the only identifiable peaks in the ^{13}C NMR spectrum were due to TaCp″(propylene)Cl$_2$ and TaCp″(C$_2$H$_4$)Cl$_2$ in a 1:5 ratio, and 2,3-dimethyl-1-butene. The sample was distilled in vacuo at 25 °C. GLC analysis showed a complex mixture of minor products but the only significant volatile product was 2,3-dimethyl-1-butene.

A 0.170-mmol sample of Cp″Cl$_2$TaCH$_2$CHMeCH$_2$CH$_2$ in toluene-d_8 prepared as above at −35 °C was treated with ethylene (4.1 mL, 0.17 mmol) by syringe at −78 °C. The sample was maintained at −78 °C for 10 min and then warmed to −35 °C for 30 min. A ^{13}C{^{1}H} NMR spectrum at −42 °C showed no change from the previous spectrum.

An attempt to prepare the mixed metallacycle by adding 1.05 equiv of ethylene to a 0.208-mmol sample of TaCp″(propylene)Cl$_2$ in toluene-d_8 at −78 °C gave (by ^{13}C NMR at −45 °C) TaCp″(C$_2$H$_4$)Cl$_2$ (~15%), Cp″Cl$_2$TaCH$_2$CH$_2$CH$_2$CH$_2$ (~10%), and Cp″Cl$_2$-TaCH$_2$CHMeCHMeCH$_2$ (~10%); ~65% of the starting TaCp″-

(propylene)Cl_2 remained. No $Cp''Cl_2Ta\overline{CH_2CHMeCH_2CH_2}$ could be detected.

29. Thermal Decomposition of $Cp''Cl_2Ta\overline{CH_2CHMeCHMeCH_2}$. A recrystallized sample of $Cp''Cl_2Ta\overline{CH_2CHMeCHMeCH_2}$ (0.107 g, 0.227 mmol), *n*-heptane (20 μL), and toluene (0.5 mL) were placed in a septum-capped 9-mm tube which was sealed under 1 atm of N_2. After 36 h at 25 °C the solution had changed from orange to dark red. The tube was cooled and opened, and a sample was quenched by injection into a septum-capped vial containing dry O_2. GLC analysis showed 2,3-dimethyl-1-butene (0.55 equiv/Ta, identified by retention time) and several minor products, the two most abundant of which coinjected with 2-methyl-1-pentene (0.0038 equiv/Ta) and 2,3-dimethyl-2-butene (0.0032 equiv/Ta). A sealed tube decomposition that was quenched before completion (1 h) showed a similar product distribution.

Assuming that the mechanism of decomposition is that shown in Scheme II, the rate of metallacycle disappearance is $-dM/dt = 2k_1M$ where M is the concentration of metallacycle and k_1 is the rate constant for the relatively slow conversion of $Cp''Cl_2Ta\overline{CH_2CH-MeCHMeCH_2}$ into $TaCp''$ (2,3-dimethyl-1-butene)Cl_2; subsequent steps are relatively fast. In terms of the olefin concentration the integrated equation is $\ln\{([ol]_\infty - [ol]_0)/([ol]_\infty - [ol])\} = 2k_1t$.

A recrystallized sample of $Cp''Cl_2Ta\overline{CH_2CHMeCHMeCH_2}$ (0.3298 g, 0.700 mmol) was placed in a 50-mL flask equipped with a side arm and stopcock and a septum inlet adaptor with a Teflon stopcock. A nitrogen line was attached to the side arm and the flask was cooled to −78 °C. Heptane (50 μL, internal standard) and toluene (10.0 mL) were added by syringe. The mixture was warmed to 0 °C with stirring to produce an orange, homogeneous solution. A sample of the solution was withdrawn by syringe and quenched by injection into a small septum-capped vial containing dry O_2. GLC analysis showed only 0.030 equiv/Ta of 2,3-dimethyl-1-butene. This demonstrates that the metallacycle can be manipulated at low temperature with little decomposition and that the quenching procedure does not convert metallacycle into 2,3-dimethyl-1-butene. The reaction flask was transferred to a constant-temperature bath (31.5 ± 0.5 °C) and equilibrated for 5 min. Samples were withdrawn by syringe at regular intervals, quenched with O_2, and analyzed by GLC for 2,3-dimethyl-1-butene. The stopcocks on the side arm and the septum inlet adaptor were kept closed except when sampling. After 15.5 h the yield of 2,3-dimethyl-1-butene was 0.53 equiv/Ta. The olefin yield vs. time was fit to the integrated rate expression (see above) with a linear least-squares program to give k_1 (31.5 °C) = 0.012 ± 0.002 min^{-1}. The last sample was taken at 2.7 half-lives and the correlation coefficient (r^2) was 0.98. A similar experiment at 0 °C gave k_1 (0.0 °C) = 0.000 40 ± 0.000 04 min^{-1}. The last sample was taken at 0.21 half-lives and the correlation coefficient (r^2) was 0.99.

^{1}H NMR samples of $Cp''Cl_2Ta\overline{CH_2CHMeCHMeCH_2}$ were prepared in C_6D_6 (~0.1 M) at 0 °C and transferred to the probe of a JEOL FX-60Q NMR spectrometer which was maintained at a selected constant temperature. Fourier transform ^{1}H NMR spectra were collected at regular intervals and the rate of disappearance of metallacycle was monitored by integration using the integral of Me_4Si as a reference. Data were collected for a total of 1–3 half-lives and fit to the integrated rate expression (see above) using a linear least-squares program to give k_1 (°C) = 0.0015 ± 0.0002 (10.0), 0.0044 ± 0.0004 (20.0), 0.014 ± 0.001 (31.5), and 0.039 ± 0.008 min^{-1} (39.5). The correlation coefficient (r^2) was ≥0.96 for each sample. An ^{1}H NMR spectrum recorded after 48 h showed a 1:1 mixture of 2,3-dimethyl-1-butene and $TaCp''$(propylene)Cl_2. Only traces of other products were detected.

The six values of k_1 and temperature give $\Delta H^\ddagger = 18.3 \pm 1.3$ kcal mol^{-1}, $\Delta S^\ddagger = -15 \pm 4$ eu, and $\Delta G^\ddagger$ (25 °C) = 22.8 ± 2.6 kcal mol^{-1}.

30. Thermal Decomposition of $CpCl_2Ta\overline{CH_2CHMeCHMeCH_2}$. The thermal decomposition of $CpCl_2Ta\overline{CH_2CHMeCHMeCH_2}$ in mesitylene (0.10 M) at 31.0 ± 1.5 °C was followed by GLC analysis for 2,3-dimethyl-1-butene using a procedure similar to the one used for $Cp''Cl_2Ta\overline{CH_2CHMeCHMeCH_2}$. After 2 h the total yield of 2,3-dimethyl-1-butene was 0.52 equiv/Ta. A linear least-squares fit to the integrated rate equation (see above) gave $k_1 = 0.023 \pm 0.003$ min^{-1}. The last point was taken after 4.0 half-lives and the correlation coefficient (r^2) was 0.97.

^{1}H NMR spectra of $CpCl_2Ta\overline{CH_2CHMeCHMeCH_2}$ in toluene-d_8 at 40 °C showed the production of 2,3-dimethyl-1-butene as the metallacycle disappeared. A large amount of dark brown solid precipi-

tated in the NMR tube and no new toluene-soluble organometallic compounds were observed.

31. Preparation and Decomposition of $Cp''Cl_2Ta\overline{CH_2CH_2CH}(n-C_4H_9)CH_2$ and $Cp''Cl_2Ta\overline{CH_2CH_2CH}(n-C_4H_9)CD_2$. $TaCp''$-$(C_2H_4)Cl_2$ (0.0696 g, 0.168 mmol) was dissolved in 0.5 mL of toluene-d_8 and transferred to a septum-capped 5-mm NMR tube. The sample was cooled to −35 °C and 1-hexene (0.0155 g, 0.184 mmol) was added by syringe. The NMR tube was shaken several times and after 20 min the color of the solution had changed from dark red to light orange, the color of a metallacycle. The ^{13}C NMR spectrum at −46 °C showed free 1-hexene and $Cp''Cl_2Ta\overline{CH_2CH_2CH}(n-C_4H_9)CH_2$ (see Table I). The sample was stored at 0 °C for 24 h; the ^{13}C NMR recorded at −45 °C showed free 1-hexene, the mixed metallacycle, a trace of $Cp''Cl_2Ta\overline{CH_2CH_2CH_2CH_2}$, and some small unidentified peaks. Disproportionation or decomposition must be slow at this temperature because the major component is still the mixed metallacycle. After 3 days at 25 °C the only peaks which could be identified in the complex ^{13}C NMR spectrum were those due to $TaCp''(C_2H_4)Cl_2$. GC/mass spectral analysis of the mixture showed a major organic product of formula $C_{12}H_{24}$ (parent ion, 168) (vide infra).

$Cp''Cl_2Ta\overline{CH_2CH_2CH}(n-C_4H_9)CD_2$ was prepared analogously using 1,1-dideuteriohex-1-ene. The ^{13}C NMR spectrum was identical with that of the undeuterated compound except that the C_α peak at 81.6 ppm was unobservable (see Table I) because of deuterium coupling and loss of the nuclear Overhauser effect. The sample was stored at 0 °C for 24 h. A ^{13}C NMR spectrum at −45 °C showed no change other than a small amount of disproportionation to give $Cp''Cl_2Ta\overline{CH_2CH_2CH_2CH_2}$. There was no evidence for scrambling of deuterium to other positions in the metallacycle ring. The sample was stored at 25 °C for 36 h and distilled in vacuo at ≤70 °C. The volatile products were analyzed by GC/mass spectrum (vide infra).

32. Mass Spectroscopy of the 1-Hexene Dimers. An authentic sample of the d_4 dimer of 1,1-dideuteriohex-1-ene was prepared by a catalytic dimerization of 1,1-dideuteriohex-1-ene with $TaCp''$-$(C_6H_5CH=CH_2)$ at 50 °C.[14,21]

Gas chromatography/mass spectroscopy was recorded on a Hewlett-Packard 5990A GC/MS. The parent ion of the major 1-hexene dimer was ~3% of the base peak. Mass spectra were recorded by scanning the region of the parent ion and automatically subtracting the background with spectrum manipulation programs. Five scans were recorded for each peak to ensure that no fractionation of compounds containing different isotopes was occurring; the figures given are average values. Major 1-hexene dimer from $Cp''Cl_2$-$TaCH_2CH_2CH(n-C_4H_9)CH_2$ (authentic d_0 dimer): 166 (1.0), 167 (1.0), 168 (100), 169 (13.2), 170 (1.5), 171 (<1.0), 172 (1.5), 173 (<1.0). Major dimer from $Cp''Cl_2TaCH_2CH_2CH(n-C_4H_9)CD_2$: 168 (1.1), 169 (<1.0), 170 (1.5), 171 (3.4), 172 (100), 173 (14.1). Authentic d_4 dimer: 168 (1.0), 169 (<1.0), 170 (1.3), 171 (3.2), 172 (100), 173 (13.8).

Within the experimental error of these measurements, the major 1-hexene dimer obtained from decomposition of Cp''-$Cl_2Ta\overline{CH_2CH_2CH}(n-C_4H_9)CD_2$ is exactly the same as the major dimer prepared catalytically and is nearly entirely d_4.

33. Characterization of $TaCp''Cl_3(PMe_3)$ and $TaCp''Cl_4(PMe_3)$. PMe_3 (60 mg, 0.8 mmol) was added to a suspension of 260 mg of $TaCp''Cl_3$ (see 13) in 10 mL of toluene to give a red solution from which red crystals could be obtained at −30 °C (0.17 g, 55%). They are very soluble in chlorobenzene but no ^{1}H NMR spectrum could be observed. At 298 K an EPR spectrum showed an eight-line pattern ($I = 7/2$ for ^{183}Ta, 100% abundant) with $g = 1.88$. We could see no coupling to ^{31}P. IR (cm^{-1}, Nujol): 1291 (m), 1286 (sh), 1026 (m), 968 (s), 950 (sh), 739 (m). Mass spectrum m/e (rel intensity): 421 (5.2, $TaCp''Cl_3$), 385 (7.9, $TaCp''Cl_3$–HCl), 349 (6.2, $TaCp''Cl_3$–2HCl), 135 (8.9, C_5Me_5), 76 (54.4, PMe_3) 61 (100.0, PMe_3–Me). All ions containing Cl showed the expected isotopic envelope.

$TaCp''Cl_3(PMe_3)$ dissolves readily in $CDCl_3$ to give a red solution which rapidly (~2 s) turns yellow. An ^{1}H NMR spectrum of this solution showed it to contain $TaCp''Cl_4(PMe_3)$.

$TaCp''Cl_4$ was prepared by adding 0.44 mL of a 4.58 M solution of HCl in ether (2.00 mmol) to 1.0 g of $TaCp''(CH_2CMe_3)Cl_3$ (2.00 mmol) in 50 mL of toluene at 0 °C. Small, yellow crystals of sparingly soluble $TaCp''Cl_4$ formed slowly during 24 h at room temperature, 0.36 g (39%).

Anal. Calcd for $TaC_{10}H_{15}Cl_4$: C, 26.22; H, 3.30; Cl, 30.96. Found:

C, 26.61; H, 3.60; Cl, 30.83. ^{1}H NMR (τ, chlorobenzene): 7.66 (s). IR (cm^{-1}, Nujol): 1480 (m), 1425 (m), 1019 (m), 803 (w), 724 (w).

A sample of TaCp''Cl$_4$ dissolved in C$_6$D$_6$ upon addition of 1 equiv of PMe$_3$ [^{1}H NMR (τ, C$_6$D$_6$): 7.78 (s, C$_5$Me$_5$), 8.46 (d, PMe$_3$, $^2J_{PH}$ = 10 Hz)]. A solution containing TaCp''Cl$_4$(PMe$_2$Ph) could be prepared similarly [^{1}H NMR (τ, C$_6$D$_6$): 2.43 (m, 2, H$_o$, PMe$_2$*Ph*), 3.00 (m, 3, H$_m$ and H$_p$, PMe$_2$*Ph*), 7.80 (s, 15, C$_5$Me$_5$), 8.07 (d, 6, P*Me*$_2$Ph, $^2J_{PH}$ = 10 Hz).

References and Notes

(1) (a) NSF Predoctoral Fellow, 1975–1978. (b) Camille and Henry Dreyfus Teacher–Scholar, 1978–1983.
(2) (a) The preferred nomenclature (according to IUPAC[2b]) is metallacyclopentane,[2c,d] not the heretofore more often used metallocyclopentane. The types we will be talking about contain only C and H in the MC$_4$ ring. Perfluorometallacyclopentane complexes can be made from C$_2$F$_4$ and have been known for some time.[2e] But like most perfluoro molecules their properties and reactions only distantly resemble those of their perprotio analogues. (b) "IUPAC—Nomenclature of Organic Chemistry", 3rd ed., Butterworth, London, 1971, rule B-4.1. (c) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7416. (d) Young, G. B.; Whitesides, G. M. *ibid.* **1978**, *100*, 5808. (e) Treichel, P. M.; Stone, F. G. A. *Adv. Organomet. Chem.* **1964**, *1*, 143.
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(13) It has been known for several years that Ni(0) complexes will catalytically dimerize norbornadiene, methylenecyclopropane or 3,3-dimethylcyclopropene to cyclobutanes, and the connection between metallacyclopentane complexes of these olefins and the dimerization reaction has been demonstrated. (See ref 2c, 4, and 12 and references cited therein.)
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(31) Whitesides[32] has demonstrated that the rate which limits the overall rate of decomposition of Pt(PPh$_3$)$_2$(Bu)$_2$ in the absence of added PPh$_3$(L) is the rate at which Pt(PPh$_3$)(Bu)$_2$ forms from Pt(PPh$_3$)$_2$(Bu)$_2$. In the presence of PPh$_3$ it is the rate at which LPt(H)(Bu)(butene) loses butane (presumably irreversibly). It must also be true that k_{-2} is larger than k_3 in order to observe the deuterium scrambling in L$_2$Pt(Bu)$_2$-d_x. But there is still no data which tells us whether β-hydride elimination or reductive elimination is *easier*; i.e., whether k_3 is larger or smaller than k_2. The unimolecular rate constant for the reductive elimination of alkane from Pt(H)(R)(PPh$_3$)$_2$, a compound which is closely related to "Pt(H)(butene)(Bu)(PPh$_3$)$_2$" (see above), has recently been measured.[33] At -25 °C it is 4.5 × 10^{-4} s^{-1}. (See references in ref 33, 7b, and 7c for other discussions and examples of reductive elimination.)

$$L_2Pt(Bu)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} LPt(Bu)_2 + L$$

$$LPt(Bu)_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} LPt(H)(butene)(Bu) \xrightarrow[-butane]{k_3} \text{"LPt(butene)"}$$
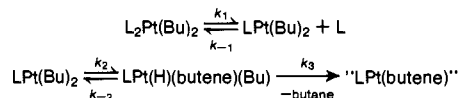
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