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TANTALLABICYCLOALKANE COMPLEXES AND THEIR USE AS CATALYSTS FOR THE CYCLIZATION OF α,ω-DIENES

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Summary

Tantallabicycloalkane complexes have been prepared from 1,6-heptadiene, 1,7-octadiene, and 1,8-nonadiene. The first is all *cis* about the common C—C bond, the second is a mixture of *cis* and *trans* isomers, and the third is all *trans*. The third decomposes at room temperature to give 2-methylmethylenecycloheptane. In the presence of excess 1,8-nonadiene, 2-methylmethylenecycloheptane is formed catalytically. Tantallabicycloalkane complexes with more than 9 carbon atoms could not be prepared and no other catalytic cyclization reactions were successful.

Introduction

We discovered recently that Ta^{V} tantallacyclopentane complexes can be prepared by adding an α-olefin to a Ta^{III} α-olefin complex [1] and that α-olefins are dimerized to a mixture of tail-to-tail and head-to-tail dimers by these complexes [2]. We also noted briefly that an 8-tantallabicyclo[4.3.0]nonane complex can be prepared from $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ and excess 1,7-octadiene and postulated that this complex should be a catalyst for the selective cyclization of 1,7-octadiene to 2-methylmethylenecyclohexane [3]. Since $\eta^5\text{-}C_5Me_5$ tantallacyclopentane complexes proved to be superior catalysts for the dimerization of α-olefins [2], we turned immediately to the analogous $\eta^5\text{-}C_5Me_5$ tantallabicycloalkane complexes. Here we report the preparation and characterization of both the $\eta^5\text{-}C_5H_5$ and $\eta^5\text{-}C_5Me_5$ complexes and a study of the activity of the $\eta^5\text{-}C_5Me_5$ complexes for catalytically cyclizing α,ω-dienes.

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Results

The characterization of (η^5-C_5H_5)$Cl_2TaCH_2(C_6H_{12})CH_2$ *(1)*

Ta(η^5-C_5H_5)($CHCMe_3$)Cl_2 reacts with three equivalents of 1,7-octadiene in pentane to give orange, crystalline **1** in good yield. A $^{13}C\{^1H\}$ NMR spectrum of a sample at 60°C (Fig. 1c) contains two sets of five signals (one η^5-C_5H_5 signal and four ring carbon signals per set) which we ascribe to two isomers. Assignment of each type of ring carbon atom (α, β, γ, or δ) was based on peak multi-

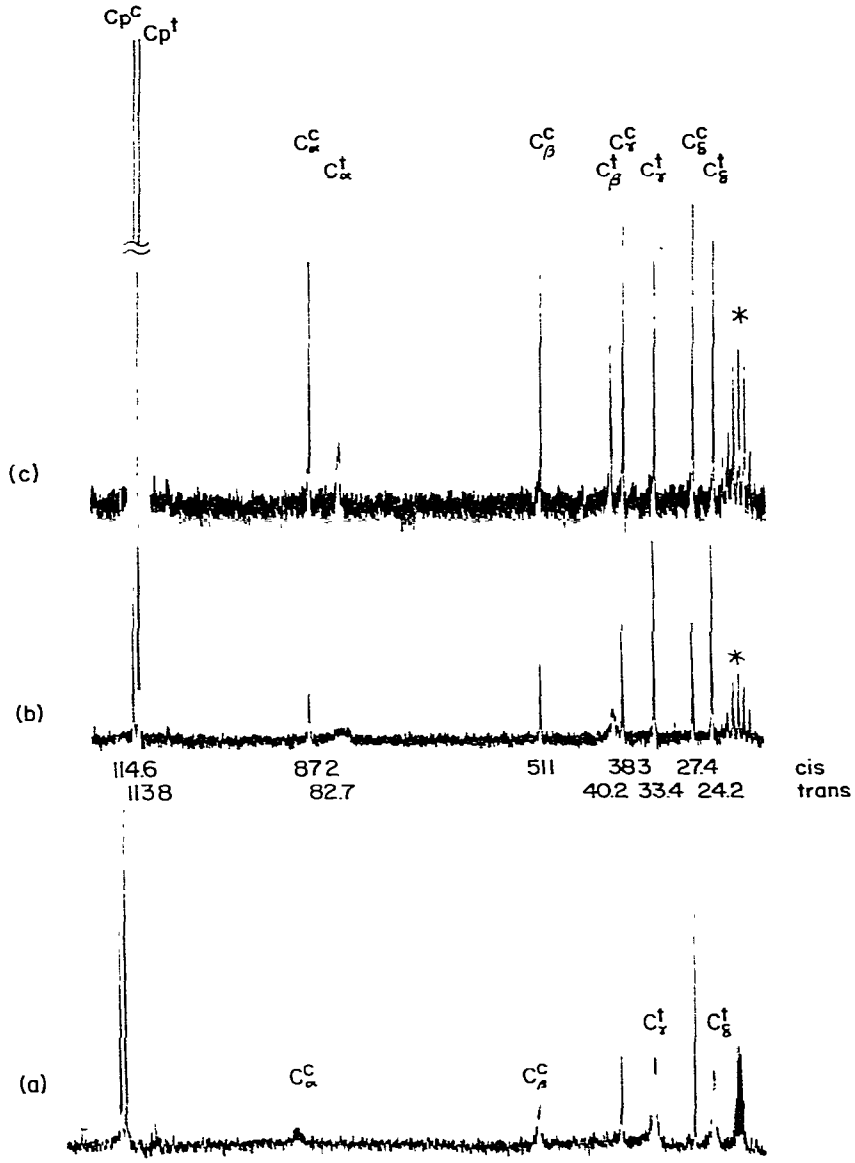


Fig. 1. The $^{13}C\{^1H\}$ NMR spectrum of a mixture of *cis*- and *trans*-**1** in toluene-d_8 (*): (c) at 22.63 MHz, 60°C; (b) at 22.63 MHz, 37°C; (a) at 67.89 MHz, 5°C (different sample; note slightly different scale).

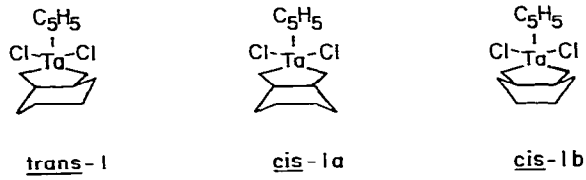


Fig. 2. *cis* and *trans* forms of 1.

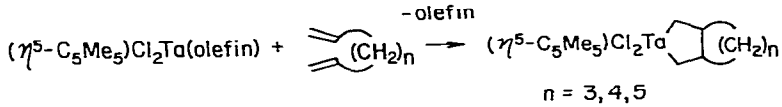
plicity in the gated decoupled spectrum and comparison of chemical shifts with those for the analogous tantallacycles made from acyclic olefins [1]. At 37°C (Fig. 1b) the signals for the α- and β-carbon atoms in one isomer begin to broaden and at 5°C (Fig. 1a) they have collapsed into the baseline. At this temperature, the signals for the γ- and δ-carbon atoms of this isomer also begin to broaden. At —36°C (67.89 MHz) two α-carbon signals of equal area appear at 69.1 and 96.0 ppm. Therefore, we assign the *trans*-configuration about the common C—C bond to this isomer (Fig. 2). At most temperatures the ring in asymmetric *trans*-**1** is turning over rapidly on the NMR time scale by what we believe to be a pseudorotation-type process analogous to that observed in tantallacyclopentane complexes made from α-olefins [1], thereby averaging C_α with C_α', C_β with C_β', etc.

The other "isomer" we believe is "*cis*-**1**", a mixture of *cis*-**1a** and *cis*-**1b** (Fig. 2). At high temperatures only average signals are seen due to the fact that the pseudorotation-type process interconverts the two forms. Freezing out this pseudorotation process is more difficult; at 5°C (Fig. 1a) the α-carbon atom and β-carbon signals are just beginning to broaden. All the average ring carbon resonances for "*cis*-**1**" eventually collapse at lower temperatures but the new resonances for *cis*-**1a** and *cis*-**1b** do not sharpen sufficiently at —36°C (68.79 MHz) to confirm their identity. However, by ^{1}H NMR at —60°C we did see the η^5-C_5H_5 resonance for the *cis* isomer split into two in about a 2 : 1 ratio. By ^{13}C NMR, $\Delta G^{\neq}$ for the pseudorotation process in *trans*-**1** is 11.9 ± 0.8 kcal mol^{-1}, and by ^{1}H NMR, $\Delta G^{\neq}$ for the interconversion of *cis*-**1a** and *cis*-**1b** is 11.5 ± 0.6 kcal mol^{-1}.

We believe that *trans*-**1** and *cis*-**1** interconvert readily on the chemical time scale since their ratio varies from sample to sample and with sample history. For example the spectra shown in Figures 1b and 1c were recorded on the same sample, first at 37°C, then at 60°C; the *trans*/*cis* ratio decreases from about 2 : 1 to about 1 : 1. This may be due in part to selective decomposition of the *trans* isomer. However, in another fresh sample the *trans*/*cis* ratio was about five by ^{13}C NMR. So far, we have not found any conditions which yield the *trans* or the *cis* isomer in pure form.

η^5-C_5Me_5 tantallabicycloalkane complexes

7-Tantallabicyclo[3.3.0]octane (**2**), 8-tantallabicyclo[4.3.0]nonane (**3**), and 9-tantallabicyclo[5.3.0]decane (**4**) complexes can be prepared by adding 1,6-heptadiene, 1,7-octadiene, and 1,8-nonadiene, respectively, to Ta(η^5-C_5Me_5)-(olefin)Cl_2 (**1**) (olefin = cyclooctene, for example, eq. 1). The first (**2**) is the least soluble and most stable. Its ^{13}C NMR spectrum shows it to consist of only



(1)

one isomer. The second (3) is entirely analogous to 1. By ^{13}C NMR we see the appropriate signals for *trans*-3 and *cis*-3. The third (4), however, has only been prepared and observed in situ; by ^{13}C NMR it is all *trans*.

The stabilities of 2, 3, and 4 vary markedly. 2 does not decompose significantly at 120°C in chlorobenzene but 3 decomposes at ca. 100°C in one hour to give 2-methylmethylenecyclohexane in 75% yield. No other organic products could be observed by GLC and the organometallic product(s) could not be characterized. 4 is the least stable, on the order of a tantallacycle prepared from an acyclic olefin like 1-pentene [1,2]. It decomposes at 25°C to give a mixture of 2-methylmethylenecycloheptane and linear oligomers. This decomposition is better studied in the presence of excess diene so that the products are formed catalytically (see below). The main point is that the rate of decomposition of 4 must differ substantially from that of 2. If we postulate that 2 would decompose at ca. 160°C at the same rate as 4 does at 30°, and that the rate of decomposition of 4 doubles every 10° (i.e., $E_a \approx 12$ kcal at 300 K), then the rate of decomposition of 4 would be ca. 10^4 times that of 2 at the same temperature.

We have not been able to prepare bicyclic complexes from 1,5-hexadiene and α,ω-dienes with ten or more carbon atoms. 1,5-Hexadiene reacts with $Ta(\eta^5\text{-}C_5Me_5)(styrene)Cl_2$ to give an insoluble orange-yellow solid which we believe is most likely a polymeric tantallacyclopentane species.

Cyclization of α,ω-diolefins

We mentioned [3] that 1 will catalytically convert 1,7-octadiene into a complex mixture of C_8H_{14} hydrocarbons. We felt that 1 decomposed under the reaction conditions to give species which were olefin isomerization catalysts and therefore did not attempt to confirm which of the C_8H_{14} isomers were cyclic (2-methylmethylenecyclohexane and isomers), if any, and which were

TABLE 1

YIELDS OF 2-METHYLMETHYLENECYCLOHEPTANE [a]

Run	Catalyst (m*M*)	Yield (%)	Comments
1	10.7	83 [b]	
2	5.9	70	
3	5.4	70	0.5 equivalents styrene added
4	9.7	62	10 equivalents styrene added
5	22	90 [c]	
6	22	54 [d]	10 ml C_6H_6
7	14.4	62	6 equiv/h addition rate [e]
8	13.3	90	1 equiv/h addition rate [e]

[a] Catalyst = $Ta(\eta^5\text{-}C_5Me_5)(styrene)Cl_2$ in 20 ml C_6H_6, unless otherwise specified. $T = 60 \pm 1$°C. A total of 10 equiv. 1,8-nonadiene added neat by syringe pump at a rate of ca. 15 equiv diene per hour unless otherwise specified. Yields are ±5%. [b] 84% in an identical run. [c] 85% in a run using 20 m*M* catalyst. [d] 57% in an identical run. [e] $Ta(\eta^5\text{-}C_5Me_5)(cyclooctene)Cl_2$ catalyst.

linear isomers of 1,7-octadiene. Instead we proceeded to study cyclization of 1,7-octadiene with 3.

At 110°C in chlorobenzene, 3 (20 m*M*) will convert 10 equivalents of 1,7-octadiene into 1.2 equivalents of 2-methylmethylenecyclohexane and 9.8 equivalents of oligomers in 12 hours. We could not substantially improve the yield of cyclized product by varying the temperature, catalyst concentration, and diene concentration, or by adding the diene very slowly by syringe pump.

The cyclization of 1,8-nonadiene was more successful. If 10 equivalents of 1,8-nonadiene are added to $Ta(\eta^5\text{-}C_5Me_5)(styrene)Cl_2$ (7.7 m*M*) in 20 ml of benzene, 68% of the diene is converted into 2-methylmethylenecycloheptane and 32% into oligomers in 6 hours. If the total reaction volume is halved the amount of cyclized product decreases to 40%.

Table 1 shows the results of several cyclization reactions of 1,8-nonadiene in benzene at 60°C using a syringe pump to add the diene. The results for runs 1, 2, and 5 suggest that the amount of cyclization is proportional to the total amount of catalyst present. Slowing the rate of addition of diene also increases the yield of cyclized product (run 8 vs. 7). Finally, for a given amount of catalyst and rate of olefin addition, use of more solvent leads to higher cyclization yields (run 5 vs. 6). Under some conditions we actually see by GLC what we believe is the tail-to-tail dimer of 1,8-nonadiene increase and decrease during the course of the reaction, but have not yet confirmed its identity.

We have tried repeatedly to extend these catalytic cyclization reactions to α,ω-dienes containing ten to fourteen carbon atoms. In all cases, we observed only oligomers.

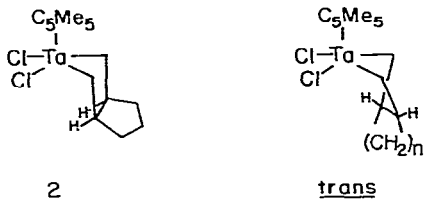
Discussion

Relatively few metallabicyclo[4.3.0]nonane complexes have been prepared from 1,7-octadiene. The biscyclopentadienyl-titanium [5] and -zirconium complexes [6,7] are, like 3, mixtures of *cis* and *trans* isomers. The relative thermodynamic stabilities * of these bicyclic systems therefore resemble those of the parent hydrocarbon [8]. A bistriphenylphosphine-nickel complex, however, was shown to be solely the thermodynamically more stable *trans* isomer [9]. We have no good explanation for this difference other than to note that an energy difference between *cis* and *trans* forms on the order of 2—3 kcal is enough to make one predominate.

The fact that 2 is all *cis* is also similar to the findings for the parent hydrocarbon [8]. A bispentamethylcyclopentadienyl zirconium complex is also all *cis* [6]. The all *trans* configuration of 4, however, differs from the parent hydrocarbon in which the energies of the *cis* and *trans* forms of the parent hydrocarbon are about equal [8].

The structure of 2 [10] was shown to be *cis* with the C_5 ring in the *exo* position (pointing away from the metal, Fig. 3). The *endo* β-hydrogen atoms, therefore, would seem to be in a position to transfer to the metal, especially

* It is likely that the *cis*/*trans* ratio in these systems is thermodynamically controlled. Some evidence is the fact that the ratio of *trans*-3 to *cis*-3 is about one at 60°C, but greater at lower temperatures, depending on sample history (see text).



2 trans

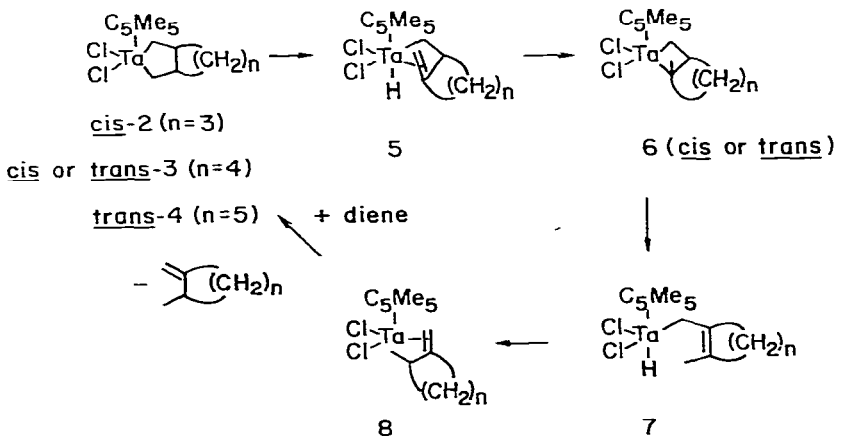
Fig. 3. *cis* and *trans* bicyclic forms.

since the TaC_4 ring is so sharply bent. (The angle between the $TaC_\alpha C_\alpha$ plane and the $C_\alpha C_\alpha C_\beta C_\beta$ plane is 123°.) This conformation is quite similar to that in the analogous unsubstituted tantallacyclopentane complex where the angle between the $TaC_\alpha C_\alpha$ plane and the $C_\alpha C_\alpha C_\beta C_\beta$ plane is 116° [10]. Each contrasts with the puckered but roughly planar configuration of the MC_4 ring in some Pt [11], Ni [12], Co [13], or Rh [13] metallacyclopentane complexes. Two explanations seem plausible. The ring is bent because the C_α—Ta—C_α angle is forced to be so small (72°), or the 14 electron metal is attracting electron density from the $C_\alpha C_\beta$ bonds. The latter is attractive since we have found that alkylidene ligands in certain Ta and Nb complexes are severely distorted because (we propose) the metal attracts electron density from the CH_α bond [14]. The crucial question is whether a 7° larger $TaC_\alpha C_\alpha/C_\alpha C_\alpha C_\beta C_\beta$ angle in 2 (vs. that in $(\eta^5\text{-}C_5Me_5)Cl_2TaCH_2CH_2CH_2CH_2$) is enough to account for the far greater stability of 2 toward β-hydride elimination (see below).

The gross features of the structure of a *trans* complex should be similar to those of 2 but the TaC_4 ring is likely to be skewed (Fig. 2). This skewing may place the *endo* β-hydrogen atom significantly closer to the metal, where it could transfer to the metal more easily. Such a conformational difference could help explain the greater stability of *cis*-2 relative to *trans*-4. This line of reasoning could also lead to the hypothesis that any given *trans* complex will be more prone to β-hydride elimination than the corresponding *cis* complex.

We assume that the mechanism of decomposition of these bicyclic complexes is analogous to that proposed for the monocyclic species [2]. The first step is β-hydride elimination to give an alkenyl hydride complex, 5 (Scheme 1). The

SCHEME 1.



second step is readdition of the Ta—H bond to the double bond to give a tantallacyclobutane complex, **6**. The third step is β-elimination to give a terminal allyl hydride complex, **7**. The fourth step is readdition of the Ta—H bond to the double bond to give the olefin complex, **8**, from which the product is rapidly displaced by more diene. This catalytic cycle competes with a version which yields oligomers. Unfortunately, we cannot make any proposals concerning the different rates of forming and decomposing **6** based on (inter alia) whether it is *cis* or *trans*, since we cannot be certain that the C=C bond in **5** remains coordinated to the metal. However, at least we can say that when $n = 5$, **6** will be significantly less strained than when $n = 3$, and the rate of forming **6** from *trans*-**4**, therefore, could be significantly faster than the rate of forming **6** from *cis*-**2**. This is at least as plausible an explanation of why *cis*-**2** is especially stable as the proposal above that *trans* complexes are in general more prone to β-elimination due to skewing of the TaC_4 ring.

cis-**3** and *trans*-**3** can interconvert in two ways. The most obvious is for the C_β—C_β bond to break and one end of the diene to dissociate. This seems reasonable based on our results for forming tantallacyclopentane complexes from acyclic α-olefins [1,2]. A second way is for the double bond in **5** to dissociate and bond to the metal through its other face before the hydride adds back to the β-carbon atom. At this time, we have no reason to favor one explanation over the other.

The rate of forming a mixture of tail-to-tail and head-to-tail dimers of $RCH{=}CH_2$ does not vary by more than a factor of about three as the size and length of R increases, in spite of the fact that the type switches over from tail-to-tail when R = methyl to head-to-tail when R = CH_2CMe_3 [2]. Therefore, the rate of forming oligomers of α,ω-dienes probably varies little with chain length. Since the rate of decomposition of tantallabicycles evidently is never greater than that of a tantallacycle made from two dienes, cyclization can be competitive only when formation of the tantallabicycle is favorable. As in purely organic systems [8], this appears to be when $n = 3$, 4 or 5, i.e. when five, six or seven-membered rings form. But the tantallabicycles from 1,6-heptadiene and 1,7-octadiene do not rearrange readily to product. Only the tantallabicycle made from 1,8-nonadeine is still favorable, and rearranges at a rate on the order of the tantallacycles made from two dienes, so that only this cyclization is successful.

Experimental

General procedures can be found elsewhere [1]. $Ta(\eta^5\text{-}C_5Me_5)(propylene)Cl_2$ [1], $Ta(\eta^5\text{-}C_5Me_5)(cyclooctene)Cl_2$ [1], $Ta(\eta^5\text{-}C_5Me_5)(styrene)Cl_2$ [1], and $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ [4] were prepared by published procedures. Yields of organic products were determined using the internal standard method and calculated response factors (proportional to molecular weight).

Preparation of $(\eta^5\text{-}C_5H_5)Cl_2Ta\overline{CH_2CH(CH_2)_4CH}CH_2$ *(1)*

$Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ (2.00 g, 5.17 mmol) and 1,7-octadiene (1.65 g, 15.0 mmol) were combined in 40 ml of pentane and stirred for 24 h. The mixture was filtered to give an orange solid which was dissolved in 15 ml of toluene.

Pentane was added until a small amount of solid precipitated, and the solution was filtered. The filtrate was cooled to −30°C to give 1.03 g of orange, crystalline product. All filtrates were combined and concentrated in vacuo. Addition of pentane and cooling to −30°C gave a second crop of 0.40 g (total yield 65%).

We also prepared 1 in low yield by stirring (η^5-C_5H_5)Cl_2TaCH$_2$CH$_2$CH$_2$CH$_2$ [1] with 3 equiv. of 1,7-octadiene in toluene for 24 h.

Anal. Found: C, 36.20; H, 4.65; Cl, 16.69. $TaC_{13}H_{19}Cl_2$ calcd.: C, 36.56; H, 4.48; Cl, 16.60%. ^{1}H NMR (δ, ppm, toluene-d_8): 5.69 (s, 5, Cp_{cis}), 5.68 (s, 5, Cp_{trans}), 3.21 (br, s, 1), 0.50—2.30 (m, 13, remaining tantallacycle protons). ^{1}H NMR (δ, ppm, toluene-d_8, −60°C): 5.39 (s, Cp_{cis}), 5.26 (s, Cp'_{cis}), 5.30 (s, Cp_{trans}), 4.07 (br, s), 0.77—2.57 (remaining tantallacycle protons). ^{13}C{^{1}H} NMR (ppm, toluene-d_8, 22.63 MHz, 60°C): 24.2 (C_δ-*trans*), 27.4 (C_δ-*cis*), 33.4 (C_γ-*trans*), 38.3 (C_γ-*cis*), 40.2 (C_β-*trans*), 51.1 (C_β-*cis*), 82.7 (C_α-*trans*), 87.2 (C_α-*cis*), 113.8 (Cp_{trans}), 114.6 (Cp_{cis}) (see Fig. 1). ^{13}C{^{1}H} NMR (ppm, toluene-d_8, 67.89 MHz, −36°C, *trans* isomer only): 23.3, 25.9 (C_δ or C_γ), 32.3, 35.0 (C_γ or C_δ), 32.9, 46.6 (C_β), 69.1, 96.0 (C_α), 113.8 (Cp).

The $\Delta G^{\neq}$ of pseudorotation for the *cis* isomer was calculated from ^{1}H NMR spectra at intermediate temperatures. For Cp and Cp′, $\delta\nu = 8.4 \pm 1.0$ Hz and $T_c = 221 \pm 10$°K or $\Delta G^{\neq} = 11.5 \pm 0.6$ kcal mol^{-1}. The $\Delta G^{\neq}$ of pseudorotation for the *trans* isomer was calculated from ^{13}C NMR spectra at intermediate temperatures. For C_δ, $\delta\nu = 178 \pm 10$ Hz and $T_c = 263 \pm 10$°K or $\Delta G^{\neq} = 12.2 \pm 0.5$ kcal mol^{-1}. For C_γ, $\delta\nu = 183 \pm 10$ Hz and $T_c = 263 \pm 10$°K or $\Delta G^{\neq} = 12.2 \pm 0.5$ kcal mol^{-1}. For C_β, $\delta\nu = 930 \pm 30$ Hz and $T_c = 273 \pm 15$°K or $\Delta G^{\neq} = 11.8 \pm 0.7$ kcal mol^{-1}. For C_α, $\delta\nu = 1830 \pm 60$ Hz and $T_c = 273 \pm 18$°K or $\Delta G^{\neq} = 11.4 \pm 0.8$ kcal mol^{-1}.

Preparation of (η^5-C_5Me_5)Cl_2TaCH$_2$CH(CH$_2$)$_3$CHCH$_2$ (2)

Ta(η^5-C_5Me_5)(propylene)Cl_2 (1.3 g, 3 mmol) and 1,6-heptadiene (0.58 g, 6 mmol) were dissolved in 20 ml benzene and the resulting orange solution was allowed to stir overnight. Removal of solvent in vacuo left an orange, crystalline solid. Recrystallization from ether/pentane gave 2 in 85% yield.

Anal. Found: C, 42.50; H, 5.24. $TaC_{17}H_{27}Cl_2$ calcd.: C, 42.25; H, 5.63%. ^{1}H NMR (δ, ppm, C_6H_6): 1.8 (s, 15, C_5Me_5), 0.6—1.6 (br, 12, C_7H_{12}). ^{13}C NMR (ppm, toluene-d_8, 15 MHz, −45°C): 12.0 (q, J = 128 Hz, C_5Me_5), 24.9 (t, J = 128 Hz, C_γ), 35.9 (d, J = 126 Hz, C_β), 41.6 (t, J = 131 Hz, C_δ), 84.6 (t, J = 128 Hz, C_α), 122.0 (s, C_5Me_5).

Preparation of (η^5-C_5Me_5)Cl_2TaCH$_2$CH(CH$_2$)$_4$CHCH$_2$ (3)

This compound was prepared from 1,7-octadiene in a manner analogous to the preparation of 2. It was isolated in 90% yield (recrystallized).

Anal. Found: C, 43.30; H, 5.87. $TaC_{18}H_{29}Cl_2$ calcd.: C, 43.47; H, 5.88%. ^{1}H NMR (δ, ppm, C_6H_6): 1.9 (s, 15, C_5Me_5), 1.0—1.8 (br, 14, C_8H_{14}). ^{13}C NMR (ppm, toluene-d_8, 15 MHz, 60°C): 12.1 (q, J = 128 Hz, C_5Me_5), 25.4 (t, J = 126 Hz, C_δ-*cis*), 27.6 (t, J = 126 Hz, C_δ-*trans*), 32.5 (t, J = 128 Hz, C_γ-*cis* and *trans*), 33.4 (d, J = 131 Hz, C_β-*cis*), 35.3 (d, J = 130 Hz, C_β-*trans*), 74.3 (t, J = 132 Hz, C_α-*cis*), 80.4 (t, J = 126 Hz, C_α-*trans*), 123.3 (s, C_5Me_5, *cis* and *trans*). The peaks were assigned based on the assumption that *trans*-3 predominates; in this sample the ratio of *trans*-3 to *cis*-3 was 3 : 2.

Preparation of trans-(η^5-C_5Me_5)Cl_2TaCH$_2$CH(CH$_2$)$_5$CHCH$_2$ (4)

Ta(η^5-C_5Me_5)(styrene)Cl_2 (0.1 g, 0.2 mmol) was dissolved in a minimal amount of toluene-d_8 and the resulting purple solution was placed in an NMR tube and cooled to ~ −10°C. One equivalent of 1,8-nonadiene (0.025 g) was added and the tube was shaken until an orange solution resulted. The sample was kept at 0°C or below until the spectrum could be recorded.

^{13}C NMR (ppm, toluene-d_8, 22.5 MHz, −40°C): 11.9 (q, J = 128 Hz, C_5Me_5), 27.3, 29.1, 29.4, 30.2, 34.2, 34.4, 47.1 (C_β, C_γ, C_δ, C_α, C'_δ, C'_γ, C'_β), 73.2 (d, J = 127 Hz, C_α), 81.9 (d, J = 127 Hz, C'_α), 122.5 (s, C_5Me_5). The signals for the carbon atoms in the C_7 ring could not be assigned due to severe signal overlap in the gated proton decoupled spectrum.

Cyclization reactions

Cyclization reactions were done in oven-dried (140°C) flasks stoppered with septa of the appropriate size. Reaction temperatures were maintained to ±1°C with a precision temperature regulator (Eastern Engineering Co., New Haven, CN).

In a typical reaction, Ta(η^5-C_5Me_5)(styrene)Cl_2 (0.2 mmol) was dissolved in 10 ml benzene and 2 mmol of diene was added along with n-decane (1 mmol, internal standard). The reaction mixture was then heated to the desired temperature for several hours. Samples for GLC analysis were removed periodically by syringe and quenched with air. Residual Ta was removed by passing the sample down a short column of alumina followed by several ml of benzene rinse. Reactions were run until no diene remained. In some cases, neat diene was added at a controlled rate with a Sage 341A syringe pump (Orion Research, Inc., Cambridge, MA).

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