5610 J. Am. Chem. Soc. 1980, 102, 5610–5618

Experimental Section

The diazenium salts 1^+–3^+ BF_4^-[3] and 4^+ $CF_3CO_2^-$[21] were prepared by published methods, as were hydrazines 1H–3H.[3]

1,1-(1,5-Cyclooctyl)-2-*tert*-butylhydrazine (4H). A mixture of 4^+-$CF_3CO_2^-$ (0.4 g), sodium borohydride (0.6 g, large excess), and 50 mL of 25% aqueous NaOH was stirred for 12 h at 25 °C and extracted with ether, and the organic layer was dried with calcium chloride and magnesium sulfate and concentrated, giving **4H** as a solid which was purified by VPC.

The pulse-radiolysis equipment (1.55-MeV Van de Graaff generator at the Hahn-Meitner-Institut Berlin) with optical detection of intermediates and the 10-MHz ac conductivity technique have been described.[23] The electron pulse width could be varied; a 1-μs pulse was usually applied. The dose per pulse was typically 300 rad, corresponding to ca. 2×10^{-6} M of primary reacting radicals. Solutions were prepared according to the usual radiation chemical standards. Oxygen was removed from the solutions by bubbling with N_2. All measurements were carried out at room temperature (20–25 °C). The data obtained were digitized by a Biomation 8100 transient recorder and analyzed on line with a PDP-11 computer.

Acknowledgments. S.F.N. thanks the Hahn-Meitner-Institut staff for its hospitality and financial support.

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Selective Dimerization of Monosubstituted α-Olefins by Tantalacyclopentane Catalysts

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Abstract: β,β′-Disubstituted and α,β′-disubstituted tantalacyclopentane complexes (e.g., $Cp''Cl_2\overline{TaCH_2CHMeCHMeCH_2}$; $Cp'' = \eta^5\text{-}C_5Me_5$) are the active intermediates in the catalytic dimerization of $RCH{=}CH_2$ (R = H, Me, *n*-Pr, *n*-Hex, CH_2CHMe_2, CH_2CMe_3) to a mixture of tail-to-tail (tt) dimer (98% when R = Me) and head-to-tail (ht) dimer (100% when R = CH_2CMe_3), respectively, at rates on the order of one turnover/h at 30 °C. The corresponding $\eta^5\text{-}C_5H_5$ catalyst is not indefinitely active, probably because $Ta(\eta^5\text{-}C_5H_5)(olefin)Cl_2$ intermediates are unstable. Deuterium-labeling studies show that each tantalacyclopentane ring contracts to a tantalacyclobutane ring which then rearranges selectively to the tt or ht dimer. We propose that an alkenyl hydride complex is an intermediate in each pathway, that it forms reversibly from the tantalacyclopentane complex, that the rate of the ring contraction step may be kinetically important, and that decomposition of the tantalacyclobutane complex is fast relative to the rate at which it re-forms its alkenyl hydride precursor.

Introduction

For several years metallacyclopentane complexes[2] have been observed as intermediates in catalytic reactions in which a high-energy olefin is cyclodimerized to a cyclobutane derivative.[3] Until recently,[4] however, similar reactions of ordinary olefins had not been observed, at least partly because metallacyclopentane complexes made from them are probably not as favorable thermodynamically. In the meantime, there seemed to be no compelling reason to invoke metallacycles in olefin dimerization reactions.[5]

During our initial investigation of the reactions of ordinary olefins with $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$ we discovered that tantalacyclopentane complexes were the ultimate products.[6] Similar $\eta^5\text{-}C_5Me_5$ tantalacycles subsequently were prepared more directly from olefin complexes of the type $Ta(\eta^5\text{-}C_5Me_5)(olefin)Cl_2$.[7] Both are active catalysts for dimerizing α-olefins[8] (e.g., propylene to 2,3-dimethyl-1-butene), although we now find that only the $\eta^5\text{-}C_5Me_5$ type is stable. To our knowledge, this is the only documented example of the use of metallacyclopentane complexes as catalysts for selectively dimerizing α-olefins[9] and the only way to obtain selectively dimers of α-olefins larger than propylene by any route.[10]

Results

Dimerization of $RCH{=}CH_2$ (R = H, Me, Pr, $(CH_2)_5Me$, CH_2CHMe_2, or CH_2CMe_3). The propylene complex, TaCp″-

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(1) (a) NSF Predoctoral Fellow, 1975–1978. (b) ITP Postdoctoral Fellow (Spain), 1977–1981. (c) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1978.

(2) In this context we mean only MC_4 complexes, and only those in which the substituents, if any, are alkyl or aryl groups.

(3) (a) Fraser, A. R.; Bird, P. H.; Bezman, S. A.; Shapley, J. R.; White, R.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 597–598. (b) Katz, T. J.; Acton, N. *Tetrahedron Lett.* **1967**, *27*, 2601. (c) Binger, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 309–310. (d) Binger, P.; Doyle, M. J. *J. Organomet. Chem.* **1978**, *162*, 195–207. (e) Doyle, M. J., McMeeking, J.; Binger, P. *J. Chem. Soc., Chem. Commun.* **1976**, 376–377.

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(7) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558–4570.

(8) (a) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 1315–1317. (b) McLain, S. J.; Sancho, J.; Schrock, R. R. *Ibid.* **1979**, *101*, 5451–5453.

(9) Grubbs recently has suggested[4] that the same Ni metallacycles which give rise to cyclobutane products catalytically also yield the olefin dimers.

(10) (a) The dimerization of propylene has been studied extensively (see ref 5b, p 128, and references cited therein). A product containing essentially only 2,3-dimethylbutenes can be formed by using some Ni catalysts but it is apparently largely 2,3-dimethyl-2-butene. Very recently, a Ni catalyst which gives only 2,3-dimethyl-1-butene (at low temperatures) at a high rate has been developed.[10b] All of these catalysts are postulated to give dimers via olefin insertions into Ni–H and Ni–C bonds. (b) Wilke, G., private communication.

0002-7863/80/1502-5610$01.00/0

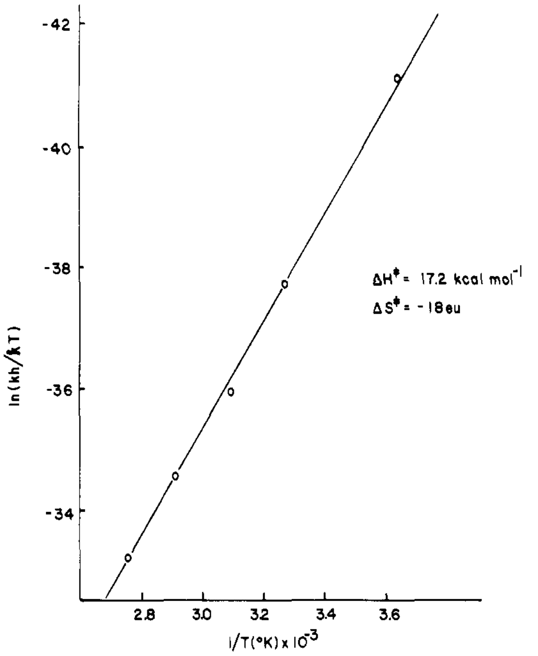


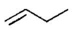
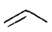
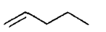
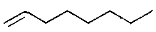
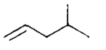
Figure 1. Plot of ln {kh/kT} vs. $1/T$ (K) for the catalytic dimerization of propylene by $Cp''Cl_2TaCH_2CHMeCHMeCH_2$ at five different temperatures.

(propylene)Cl_2 (Cp'' = η^5-C_5Me_5), is in equilibrium with the *trans*-β,β'-disubstituted tantalacyclopentane complex $Cp''Cl_2TaCH_2CHMeCHMeCH_2$, in the presence of propylene.[7] When the tantalacycle decomposes, it gives back the propylene complex quantitatively and produces 0.5 equiv of 2,3-dimethyl-1-butene,[7] the tail-to-tail (tt) dimer. Not surprisingly, therefore, 2,3-dimethyl-1-butene is formed catalytically in the presence of excess propylene. We believe that the rate of the catalytic reaction is determined by how fast the tantalacyclopentane complex decomposes since both the stoichiometric decomposition and catalytic dimerization are first order in Ta and the rate constant and thermodynamic parameters for the catalytic reaction are identical with those for the stoichiometric reaction within experimental error. For the stoichiometric reaction at 39.5 °C, k = 0.039 ± 0.008 min^{-1}, $\Delta H^‡$ = 18.3 ± 1.3 kcal mol^{-1}, $\Delta S^‡$ = −15 ± 4 eu, and $\Delta G^‡$(25 °C) = 22.8 ± 2.6 kcal mol^{-1}.[7] For the catalytic reaction at 39.5 °C, k(calcd) = 0.034 min^{-1}, $\Delta H^‡$ = 17.2 ± 0.6 kcal mol^{-1} (17.22 exact), $\Delta S^‡$ = −18 ± 2 eu (−18.5 exact), and $\Delta G^‡$(25 °C) = 22.7 ± 1.2 kcal mol^{-1}. The plot used to calculate the latter thermodynamic values is shown in Figure 1.

Two features of this reaction should be pointed out here. First, the results of the stoichiometric decomposition suggest that propylene must displace 2,3-dimethyl-1-butene rapidly from any intermediate 2,3-dimethyl-1-butene complex. This seems reasonable since complexes of disubstituted α-olefins could not be prepared.[7] Such olefins probably cannot lie in the preferred orientation parallel to the Cp'' ring for steric reasons.[11] Secondly, the fact that the plot in Figure 1 is linear suggests that essentially all the tantalum is in the form of the orange β,β'-metallacycle, even at 90 °C. This is apparent visually since at 90 °C the solution is only a dark orange, consistent with only a small amount of the more deeply colored, purple propylene complex being present. In this case, then, we can say that the rate is essentially independent of olefin concentration when there is a large excess of propylene present (50 psi). Later we will see that this is not true for all α-olefins.

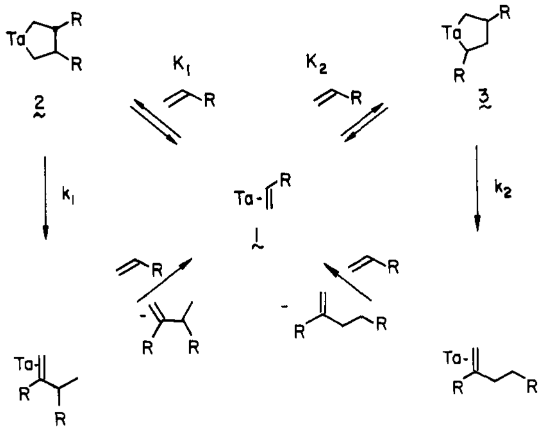
A second primary product of the propylene dimerization reaction is the head-to-tail (ht) dimer, 2-methyl-1-pentene. It is formed steadily as 2% of the product mixture. It almost certainly forms from the α,β'-dimethyltantalacycle, $Cp''Cl_2TaCHMeCH_2CHMeCH_2$, even though no α,β'-disubstituted tantalacyclopentane complex has ever been observed by ^{13}C NMR.[7] At 0 °C the amount of tt dimer is 99.3% and the amount of ht dimer is 0.7%. At 90 °C these percentages are 96.4 and 3.6, respectively.

Table I. Dimerization of Olefins in Toluene at 50 °C with $TaCp''(cyclooctene)Cl_2$[a]

olefin	product ratio tt	product ratio ht	k^b	$k_1{}^b$	K_1, M^{-1}
=		(100%)	2 ± 1	2 ± 1	
	98	2	8.7 ± 0.9	8.5 ± 0.9[c]	
	88	12	8.3 ± 0.8	7.3 ± 0.8[c]	
	86	14	7.2 ± 0.7	~7	~3[d]
	61	39	4.7 ± 0.5	~3	~3[e]
	0	100	2.6 ± 0.3	small	<0.1

[a] Initial concentrations are 0.07 (Ta) and 2.8 M (olefin). See Experimental Section for details. The cyclooctene is displaced rapidly by the olefin reactant and is inert under the reaction conditions (see text). [b] Units are min^{-1} × 10^{-2}. [c] Assuming K_1 is large and $>>K_2$. This correct value is slightly smaller than that originally reported.[8b] [d] Calculated from dependence of the rate on olefin concentration (Table II and text). The error is at least ±1. [e] Calculated from the results of a ^{13}C NMR experiment (see text). The error is at least ±1.

Scheme I. Catalytic Dimerization of $RCH{=}CH_2$



The same two dimers are observed on dimerizing several other α-olefins (Table I). The two postulated pathways by which we propose they form for a general α-olefin, $RCH{=}CH_2$, are shown in Scheme I. The overall rate of dimerization decreases as the size of R increases (the exception being ethylene, which is dimerized slowest of all) and the product composition switches over from virtually all tt dimer in the case of propylene to exclusively the ht dimer in the case of 4,4-dimethyl-1-pentene.

The product switchover was at first surprising since for 4,4-dimethyl-1-pentene only **2** was observed at 0 °C[7] and only **1** under catalytic conditions; we never saw any evidence for **3** by NMR methods. Therefore we looked for the α,β'-metallacycle of 4-methyl-1-pentene by ^{13}C NMR in a sample consisting of 0.45 mmol of $TaCp''(4\text{-methyl-1-pentene})Cl_2$ and 2.4 mmol of 4-methyl-1-pentene (~0.3 mL) in 0.30 mL of C_6D_6 at 50 °C. After 400 pulses the spectrum showed no detectable olefin complex (**1**) or α,β'-metallacycle (**3**); the only species detected were free olefin and the β,β'-metallacycle (**2**), which at this temperature showed a single average peak for interchanging C and $C_\alpha{}'$[7] at 81.3 ppm. Therefore we conclude that K_2 is small in all cases and that $[Ta]_T$ (the total amount of tantalum added to the reaction) = [**1**] + [**2**]. The rates of forming the tt dimer and ht dimer then can be

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(11) M. R. Churchill found that ethylene in $TaCp''(ethylene)Cl_2$ is oriented parallel to the Cp'' ring (unpublished results).

Table II. Effect of 1-Octene and Ta Concentration on the Rate of Dimerization of 1-Octene in Toluene at 50 °C with TaCp''(cyclooctene)Cl_2

1-octene, M	Ta, mM	k^b
1.4	18	5.8
1.4	35	6.5
1.4	70	6.3
2.8	70	7.2
5.6	70	7.7
6.4[c]	70	8.3

[a] Initial concentrations are 0.07 (Ta) and 2.8 M (olefin). See Experimental Section for details. [b] Units are 10^{-2} min^{-1}. All values are ± ca. 0.5. $k^{tt} = 0.86k$ since the percent tt dimer is 86 in each case. [c] Neat olefin.

expressed as shown in eq 1 and 2 and $dP_{total}/dt = k[Ta]_T \equiv (k^{tt} + k^{ht})[Ta]_T$.

$$\frac{dP_{tt}}{dt} = \frac{k_1K_1[ol][Ta]_T}{1 + K_1[ol]} \equiv k^{tt}[Ta]_T \qquad (1)$$

$$\frac{dP_{ht}}{dt} = \frac{k_2K_2[ol][Ta]_T}{1 + K_1[ol]} = k^{ht}[Ta]_T \qquad (2)$$

Estimates of K_1 and k_1 in three cases illustrate that both decrease as the size of the alkyl substituent increases. The estimate that $K_1 < 0.1$ at 50 °C for 4,4-dimethyl-1-pentene is based on the fact noted above, that the olefin complex is the only observable organometallic species under catalytic conditions. Actually, this upper limit probably is much too large since $K_1 \approx 1$ at 0 °C.[7] Since no tt dimer in fact forms it is reasonable to propose that k_1 is smaller than in the case of 4-methyl-1-pentene. K_1 for 4-methyl-1-pentene can be estimated by a continuation of the experiment described in the above paragraph. After 2000 pulses we saw the two olefin dimers **2** and **1** in a ratio of ca. 5, and about half the amount of monomer we started with. Since the estimated total volume is 0.7 mL, K_1 at 50 °C is on the order of 3. Therefore we can estimate that $k_1 \approx 3 \times 10^{-2}$ min^{-1}. K_1 for 1-octene was estimated from the data shown in Table II; these data illustrate that the rate of dimerization of 1-octene is not independent of the concentration of 1-octene. If we guess that K_1 is on the order of 3, then in neat olefin (6.4 M) $k_1 \approx k^{tt} = 0.86k$ or $k_1 \approx 7.1$ (units = 10^{-2} min^{-1}, as always). These values for K_1 and k_1 yield values for k^{tt} which agree fairly well with the experimental results for the three smaller concentrations of olefin (calcd for k^{tt}: 6.6, 6.3, 5.7. Found: 6.6, 6.2, 5.4).

Since the ht dimer is formed in 100, 39, and 14% yield, respectively, k_2 must be substantial in the last three cases listed in Table I. We conclude that either k_2 is always substantially larger than k_1 (but does not vary drastically) or it increases as k_1 decreases.

Some General Features of the Catalyst System. We have shown that neither the rate of the propylene dimerization reaction nor the ratio of tt to ht dimers seems affected by the type of solvent. The results were the same within experimental error in ether, toluene, decane, or chlorobenzene. Chlorinated solvents such as dichloromethane are not suitable since they react with TaCp''(olefin)Cl_2 complexes at room temperature.[7]

It is convenient in these reactions to use TaCp''(cyclooctene)Cl_2[7] as the catalyst since cyclooctene is readily displaced and inert under the reaction conditions. Several propylene dimerization reactions at 30 °C using TaCp''(cyclooctene)Cl_2 gave results identical with those using TaCp''(propylene)Cl_2. In this case, cyclooctene can be used as the internal standard.

These catalyst systems are very sensitive to air and water. In any typical run under less than rigorously water- and oxygen-free conditions, the rate decreases to near zero after about 24 h. For example, using 1.2 mmol of TaCp''(propylene)Cl_2 in 6.1 mL of decane at 45 °C, propylene (40 psi) was dimerized to ~22 mol of product in 24 h before the rate was essentially zero. Four lines of evidence suggest that the catalyst deactivation is caused by a slow, constant diffusion of oxygen or water into the apparatus. First, the metallacycle **2** is known to react rapidly with oxygen. Second, increasing the temperature of the reaction gives a larger dimerization rate and turnover number, but the catalyst deactivation takes about the same amount of time. For example, at 70 °C, the catalyst lifetime was 27 h and the turnover number was 155. Third, doubling the amount of catalyst in the 70 °C dimerization prolonged the catalyst lifetime to >27 h and increased the turnover number still further to 497. Fourth, a preparative-scale dimerization of 1-octene in which air and water were rigorously excluded gave >1200 turnovers with no apparent catalyst deactivation.

The catalyst systems probably are not long lived at higher temperatures since TaCp''(olefin)Cl_2 complexes decompose readily at 100 °C in the absence of olefin.[7] Catalyst decomposition then should be especially troublesome when the TaCp''(olefin)Cl_2 ⇄ tantalacyclopentane equilibrium lies significantly to the left (e.g., toward the end of a reaction). We have never tried dimerization reactions at >100 °C.

Table III shows some results of dimerizing propylene by modified catalysts. The rate of dimerization of propylene by the bromide complex is faster than that of the chloride complex by a factor of 2, while the monomethoxy derivatives are much poorer dimerization catalysts at 30 or 60 °C, the rates being $^1/_{40}$ and $^1/_{30}$ the rate of the dichloride complex at these respective temperatures. We conclude that the rate of propylene dimerization slows markedly as X in TaCp''(olefin)X_2 varies in the order Br > Cl ≫ OR.

In one instance we checked the effect of adding Cl^-. One equivalent of $Et_4N^+Cl^-$ dissolves in a chlorobenzene solution of TaCp''(cyclooctene)Cl_2 and the subsequent rate of dimerization using this modified catalyst is about half that of the TaCp''(cyclooctene)Cl_2 catalyst without added Cl^- (Table III).

Finally, we attempted to dimerize propylene with NbCp''($CHCMe_3$)Cl_2. This complex reacts slowly with propylene to give 55% of the expected products[6] resulting from decomposition of an intermediate metallacyclobutane complex (eq 3) but no dimerization products whatsoever. A brown precipitate formed which we assume to be a decomposition product. It could not be identified.

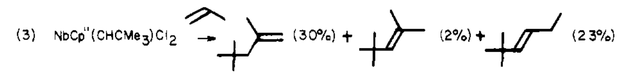
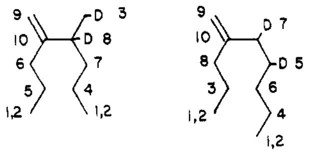


Table III. Dimerization of Propylene (40 psi)[a]

catalyst	solvent	T, °C	k^b	tt dimer	ht dimer
TaCp''(cyclooctene)Cl_2	toluene[c]	30	1.5	98	2
TaCp''(cyclooctene)Br_2	toluene	30	3.2	93	7
TaCp''(cyclooctene)Cl_2 + 1.0 $Et_4N^+Cl^-$	PhCl	30	0.9	98	2
$Cp''Cl(OMe)\overline{TaCH_2CHMeCHMeCH_2}$[d]	toluene	30	0.04		
NbCp''($CHCMe_3$)Cl_2	toluene	30	inactive[e]		
TaCp''(cyclooctene)(OMe)Cl	toluene	60	0.9		
TaCp''(cyclooctene)Cl_2	toluene	60	27		

[a] These experiments were done in a manner analogous to other dimerization reactions (see Experimental Section). [b] Units are 10^{-2} min^{-1}. [c] The rate is the same in chlorobenzene or ether. [d] This metallacycle is an isolable, yellow, crystalline complex which forms rapidly from TaCp''(cyclooctene)(OMe)Cl and propylene. [e] Total stoichiometric products = 55%; 2,4,4-trimethyl-1-pentene = 30%; 2,4,4-trimethyl-2-pentene = 2%; *trans*-2,2-dimethyl-3-hexene = 23%.

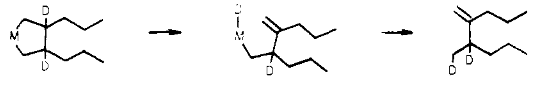


4 5

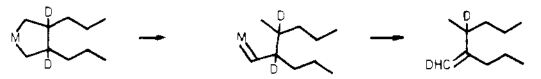
Figure 2. Dimers of 2-deuterio-1-pentene.

Deuterium Labeling Studies. The dimerization of 2-deuterio-1-pentene produced the tt and ht dimers at a substantially slower total rate; $(k_H/k_D)^{tt} = 3.3 \pm 0.7$ and $(k_H/k_D)^{ht} = 1.2 \pm 0.2$. These two dimers were isolated by preparative GLC and identified as **4** and **5** (Figure 2), respectively. We can estimate from an expanded version of the $^{13}C\{^1H\}$ NMR spectrum of the tt dimer (**4**) shown in Figure 3 that C_3 and C_8 are labeled >90% as shown. (The regioselectivity is probably a good deal better than that as we will show later for a slightly different case.) The labeling in **4** and the fact that $k_H/k_D = 3.3$ are entirely consistent with a β-elimination pathway (eq 4) and augur against an α-abstraction pathway[14] such as that shown in eq 5. However, labeling in the ht dimer (**5**) is *not* consistent with a reductive elimination pathway (eq 6). A *proton* must be lost from a β-carbon atom (k_H/k_D = 1.2) to give an internal alkenyl hydride which then collapses to a metallacyclobutane complex (eq 7). This is the same type of metallacyclobutane complex which we postulated forms when an olefin adds to $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$. In this monocyclopentadienyl system it rearranges almost exclusively to the type of product shown.[6] What this experiment does not tell us, however, is whether the β,β′-disubstituted metallacyclopentane ring also contracts to a metallacyclobutane ring (α,α,β-trisubstituted) since the results would be indistinguishable from those obtained by reductive elimination (eq 4).

(4)



(5)



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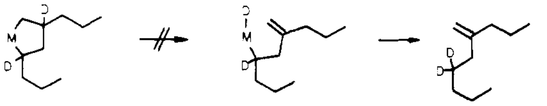
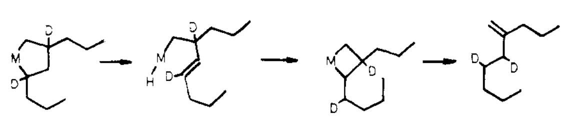
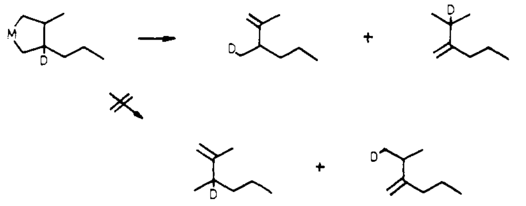


(7)



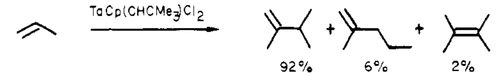
In order to determine if a β,β′-disubstituted MC_4 complex also contracts we codimerized propylene with 2-deuterio-1-pentene. The tt codimers (~90% of the codimer mixture) were isolated by preparative GLC and examined by ^{13}C NMR (Figure 4a). All peaks for isomer A can be assigned unambiguously. The deuterium is located on carbon A_4. We can determine the regioselectivity of this reaction since an expanded version (Figure 4b) shows a small peak for A_4 with a proton attached ($A_4(H)$). Based on what the peak height for $A_4(H)$ should be we estimate that only 2–3% $A_4(H)$ is present. This was confirmed by adding 5% of all-protio A and comparing the peak for $A_4(H)$ in a similar spectrum with that in Figure 4b. Therefore, this reaction is at least 97% regioselective. The result for isomer B is less certain since the assignments for B_6 and B_7 could be reversed, but at least the result is not the alternative with deuterium bound to B_3. However, we believe that deuterium *is* bound to B_6 (Figure 4c) since there is no obvious way how it could turn up bound to B_7. We cannot estimate the regioselectivity as easily for B as for A owing to the inherent greater intensity of a methyl carbon signal; we suspect that it is equally high. These two products are not the ones expected from the reductive elimination pathway but those expected from the ring contraction pathway (eq 8). Therefore, we conclude that all $Cp''Cl_2\overline{TaCH_2CHRCHRCH_2}$ complexes also decompose via ring contraction to an α,α,β-trisubstituted metallacyclobutane complex.

(8)



Dimerization with η⁵-C₅H₅ Catalysts. We first observed tantalacyclopentane complexes and olefin dimerization when we reacted $TaCp(CHCMe_3)Cl_2$ with an olefin.[6,8] For example, when a decane suspension of $TaCp(CHCMe_3)Cl_2$ is stirred under 40 psi of propylene at 45 °C, the red solid dissolves to give an orange solution of the metallacycle and an 85% yield of 2,4,4-trimethyl-1-pentene. GLC analysis shows that *three* dimers of propylene form: 2,3-dimethyl-1-butene (92%), 2-methyl-1-pentene (6%), and 2,3-dimethyl-2-butene (2%) (eq 9). For the first few hours of the reaction, the combined absolute yield of dimers increases linearly with time. Assuming that the reaction is first order in tantalum, the rate constant for dimer formation is 0.052 min^{-1}, close to the corresponding k using $TaCp''(propylene)Cl_2$ (0.044 min^{-1}). The rate of dimerization slowly decreases as a brown precipitate forms and within 24 h the dimerization has stopped (~20 turnovers). We believe that the catalyst is deactivated largely because the $TaCp(olefin)Cl_2$ complexes are unstable,[7] but also because O_2 diffuses into the reaction as found for the $\eta^5\text{-}C_5Me_5$ catalysts (see previous section).

(9)



The ethylene metallacycle, $CpCl_2\overline{TaCH_2CH_2CH_2CH_2}$, is considerably more stable than $CpCl_2\overline{TaCH_2CHMeCHMeCH_2}$; it does not decompose to give ethylene dimers (stoichiometrically or catalytically) at 25 °C. At 80 °C in mesitylene, however, it catalyzes the dimerization of ethylene (40 psi) to 1-butene (96.6% relative yield), *trans*-2-butene (3.0%), and *cis*-2-butene (0.3%). Two other major products with formulas C_6H_{12} were identified by GC/mass spectroscopy. These products are probably codimers of 1-butene and ethylene. The proportion of codimers in the mixture increases with time. After 15 h the absolute yields follow: 1-butene (22 equiv/Ta), *trans*-2-butene (0.76 equiv/Ta), *cis*-2-butene (0.11 equiv/Ta), and C_6H_{12} (5.2 equiv/Ta).

When a solution of $CpCl_2\overline{TaCH_2CH_2CH_2CH_2}$ is stirred under ethylene (20 psi) and propylene (30 psi), there is no reaction at 25 °C. Heating the mixture to 70 °C for 12 h gives 1-butene (16.4 equiv/Ta), 2,3-dimethyl-1-butene (0.53 equiv/Ta), and a codimer of ethylene and propylene (5.6 equiv/Ta). Since the propylene metallacycle is known to decompose much more rapidly than the ethylene metallacycle,[7] the ethylene metallacycle must be the major component of the reaction mixture.

The reaction of 1-butene with $TaCp(CHCMe_3)Cl_2$ yields only 1.2 equiv of 1-butene dimers (identified as C_8H_{16} by GC/mass spectroscopy) before the system deactivates. 1-Hexene gives a similar result (see Experimental Section for details).

$TaCp(CHCMe_3)Br_2$ catalyzes the dimerization of propylene at a rate which is about 2.5 times faster than the rate using $TaCp(CHCMe_3)Cl_2$ to give 89% 2,3-dimethyl-1-butene, 8% 2-methyl-1-pentene, and 3% 2,3-dimethyl-2-butene.

$NbCp(CHCMe_3)Cl_2$ reacts with propylene to give 60% of the expected 2,4,4-trimethyl-1-pentene and a brown precipitate. Not

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(12) Prepared by adding TlC_5Me_5 to $Nb(CHCMe_3)(THF)_2Cl_3$[13]: Rupprecht, G. A., unpublished results.

(13) Rupprecht, G. A.; Fellmann, J. D.; Messerle, L. W.; Rocklage, S.; Schrock, R. R. *J. Am. Chem. Soc.*, in press.

(14) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

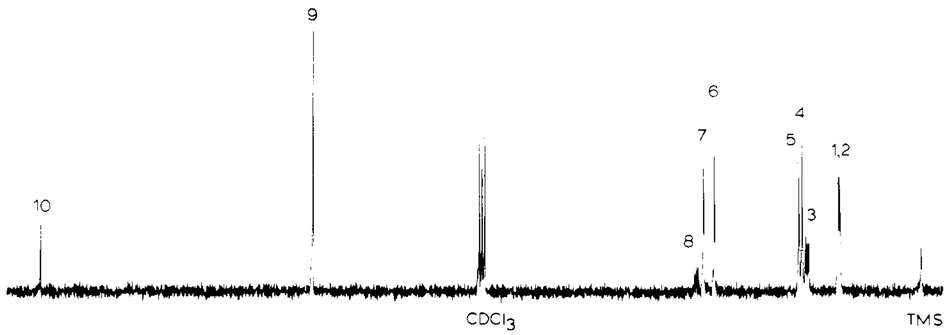


Figure 3. The 67.89-MHz $^{13}C\{^1H\}$ NMR spectrum of the tt dimer (4, Figure 2) of 2-deuterio-1-pentene.

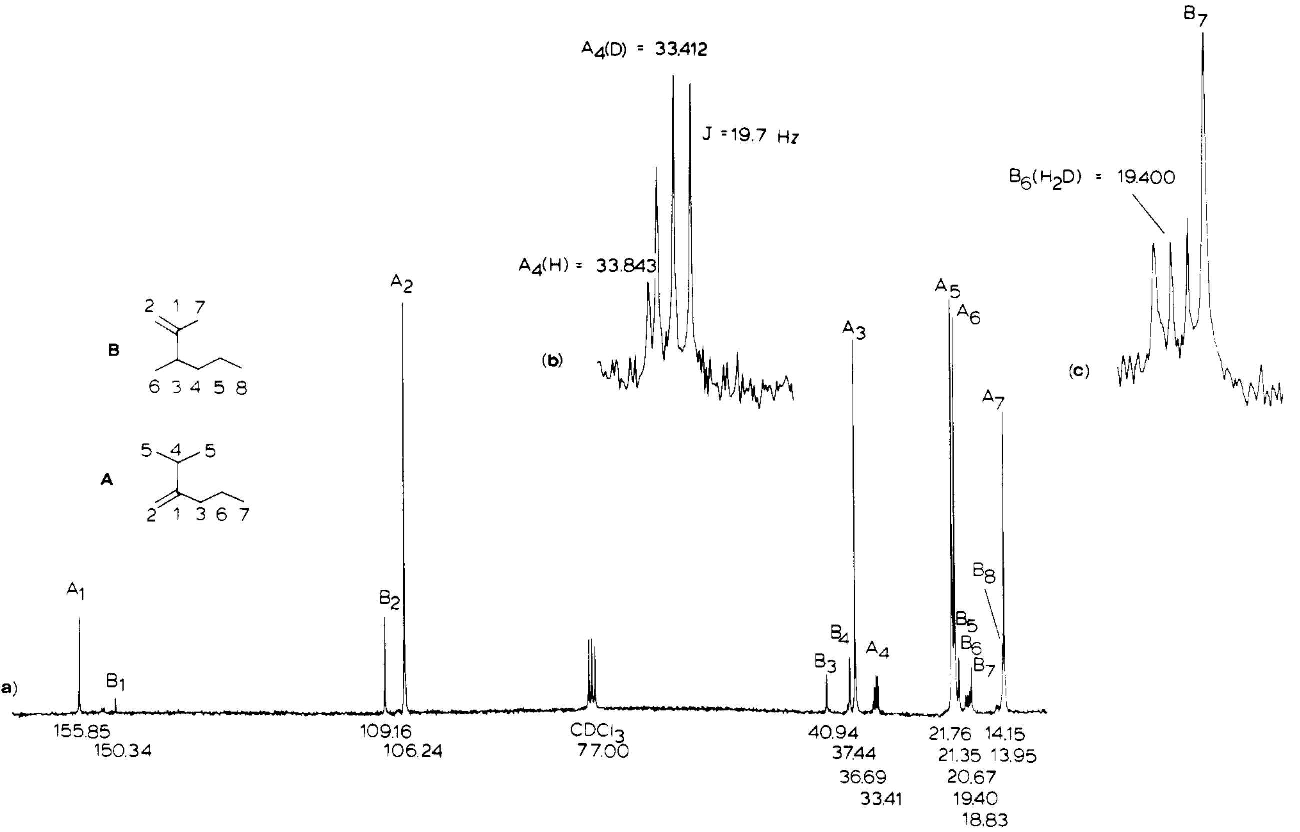


Figure 4. (a) A 67.89-MHz $^{13}C\{^1H\}$ NMR spectrum of the two tt-propylene/2-deuterio-1-pentene codimers. (b) An expansion of the peak due to carbon A_4. (c) An expansion of the peak due to carbons B_6 and B_7.

even a trace of propylene dimers could be detected in the reaction mixture by GLC.

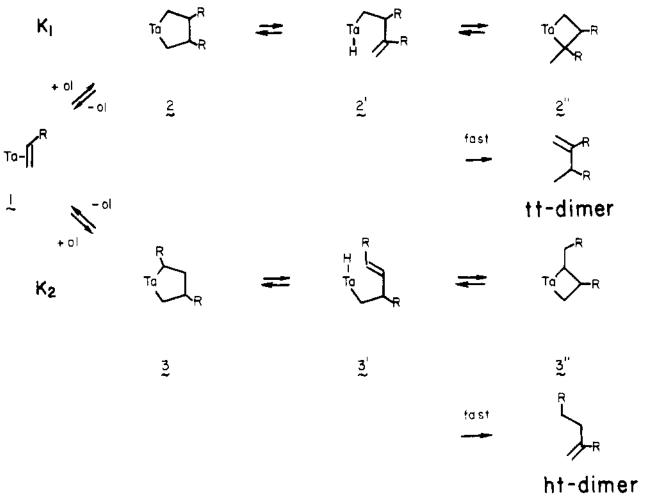
Discussion

The two competing catalytic pathways are shown in more detail in Scheme II. We prefer to propose intermediate alkenyl hydride complexes **2′** and **3′** even though we cannot strictly exclude other less precedented means of converting **2** to **2″** and **3** to **3″**. An example is a more or less concerted process in which the Ta–C_α bond cleaves as a β-hydrogen atom migrates from C_β to C_α and a new bond forms between Ta and the erstwhile C_β. We believe that the last step of each pathway is fast (see later).

Let us first consider the implications of the finding that no H/D scrambling was found in the products of the labeling experiments. For the tt dimer this implies that either the step **2″** → **2′** is slow or the step **2′** → **2** is slow, or both are slow. But if product formation from **2″** is fast, then most likely the step **2″** → **2′** is relatively slow. For similar reasons the step **3″** → **3′** probably is slow.

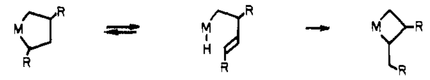
The key question in the sequence of steps yielding the tt dimer is whether the step **2′** → **2** is faster or slower than the step **2′** → **2″**. We propose that it is faster since it is probably easier to form the five-membered ring (**2**) than the more crowded, four-membered ring (**2″**). In contrast, for the ht dimer it is not as clear (based on steric considerations) that the step **3′** → **3** will be faster than the step **3′** → **3″**. Nevertheless, the ring contraction step could be kinetically important for both pathways and could even

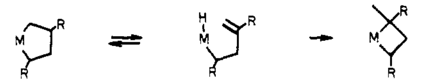
Scheme II

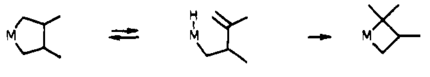


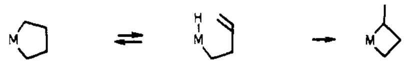
be the slowest step in some circumstances. The β-elimination step (**2** → **2′** or **3** → **3′**) could be the slowest in other circumstances, as has been postulated for other metallacyclopentane systems.[15]

The fact that a β-hydrogen atom is removed from a secondary (eq 10), not a tertiary (eq 11), carbon atom in an α,β′-tantalacyclopentane complex seems reasonable for several reasons:[16] cleavage of the secondary M–CHR bond may be accelerated for steric reasons, the secondary β proton is probably more accessible, and the α,α,α′-trisubstituted metallacycle in eq 11 is much more crowded than the α,β-disubstituted metallacycle in eq 10. But one then can rationalize the greater rate of dimerizing propylene (eq 12) vs. ethylene (eq 13) only by saying that the "rule" applies only to α,β′-disubstituted metallacyclopentane rings since the metallacyclopentane in eq 12 also must collapse to the much more crowded α,α,β-trimethyltantalacyclobutane complex.

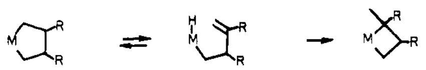
(10)


(11)


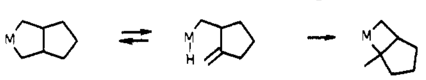
(12)


(13)


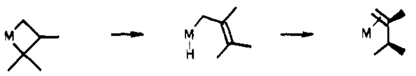
The switchover from tt dimer to ht dimer as R becomes large could be explained by a more difficult β-elimination step or greater difficulty of forming the more crowded α,α,β-tantalacyclobutane complex (eq 14 vs. eq 10). However, it is surprising that the rate of dimerizing 4,4-dimethyl-1-pentene to the ht dimer is still substantial in spite of the fact that K_2 must be quite small. Perhaps the steps **3** → **3′** and **3′** → **3″** are always relatively fast but this pathway is normally blocked by the fact that $K_1 \gg K_2$ ($dP_{ht}/dt = k_2K_2[ol][Ta]_T/(1 + K_1[ol])$). If K_1 decreases substantially and k_2K_2 does not change much, then dP_{ht}/dt for 4,4-dimethyl-1-pentene could indeed be on the order of dP_{tt}/dt in other cases, as we have found (Table I).

(14)


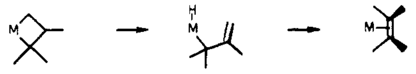
One intriguing aspect of the proposition that the ring contraction step is kinetically important is that we can then rationalize why some decompositions, such as that shown in eq 15,[8a] are so slow; the equilibrium might be much the same as it is for the propylene tantalacycle but the ring contraction is much slower since a strained bicyclic intermediate must form.

(15)


So far we have said little about the final step, the rearrangement of the metallacyclobutane ring to an olefin. It would seem illogical to postulate that this "reductive elimination" of an olefin from a σ- or π-allyl hydride intermediate is fast having postulated that reductive elimination of a butene from a butenyl hydride is slow. But, if we view the final step another way, it is actually closely related to the step in which the tantalacyclobutane complex is formed; i.e. if the metal hydride again adds relatively rapidly to the double bond in a primary σ-allyl hydride intermediate, then the final result is the same (e.g., eq 16). The primary σ-allyl would seem most likely in a relatively crowded coordination sphere.

(16)


It is interesting to consider the possibility that the 2% tetramethylethylene found in the propylene dimerization with $CpCl_2\overline{TaCH_2CHMeCHMeCH_2}$ comes about because the alternative secondary σ-allyl is more easily formed in this somewhat less crowded environment (vs. the η^5-C_5Me_5 system) and addition of M–H to it generates a tetramethylethylene complex (eq 17).

(17)


An interesting question is why β-elimination in these tantalacyclopentane complexes is so much easier than in platinacyclopentane complexes.[15] One clue may be found in the recent results of an X-ray structure of $Cp''Cl_2\overline{TaCH_2CH_2CH_2CH_2}$.[17] The MC_4 ring is *not* roughly planar and slightly puckered (as is the case in a Pt system[18]) but is sharply bent about the C_α carbon atoms away from the η^5-C_5Me_5 ring in an "open envelope" configuration. (The dihedral angle between the $TaC_\alpha C_\alpha$ and $C_\alpha C_\alpha C_\beta C_\beta$ planes is 116°.) This configuration cannot be ascribed to steric repulsion of the β-CH_2 groups by the η^5-C_5Me_5 ring. We believe that it is due either to the small C_α–Ta–C_α angle (72°) or to the metal's attracting electron density from the C_α–C_β bonds. (The latter should be compared to the interaction of the neopentylidene CH_α electrons with the metal which is postulated to account for the rather large $M{=}C_\alpha{-}C_\beta$ bond angle in several related tantalum complexes.[14,19]) In either case the rate of forming a butenyl hydride complex (possibly with the butenyl C=C bond still interacting with the d^0 metal) thereby could be accelerated significantly.

The above hypothesis might help explain why the analogous methoxide-substituted tantalacycle is so much more stable. The methoxide ligand does not withdraw as much electron density as the more electronegative chloride (or, alternatively, it adds more to the metal using its lone electron pairs, or both) so that the metal is not as electron deficient. The TaC_4 ring therefore might be flatter and the β-elimination step significantly more difficult. We hope to probe the validity of this proposal with X-ray studies of the appropriate complex in the near future.

Experimental Section

Oxygen and water were removed from propylene (Matheson CP grade) by passing it through 3 Å molecular sieves and Cr(II) on silica gel.[20] Ethylene (Matheson CP grade) was used as received. Higher olefins used for kinetic studies were dried over activated 4 Å molecular sieves and degassed by several freeze–pump–thaw cycles on a high-vacuum line. Solvents for kinetic studies were distilled from either titanocene[21] (decane, benzene, toluene) or Na/benzophenone (toluene, ether). $TaCp''(olefin)Cl_2$[7] and $TaCp(CHCMe_3)X_2$[22] (X = Cl or Br) complexes were prepared as described in the literature. Relative GLC responses were assumed to be proportional to molecular weight in reactions where no authentic products were available.

(1) Preparation of TaCp″(cyclooctene)Br₂. $TaCp''(propylene)Br_2$ was prepared in a manner analogous to that used to prepare the chloro analogue,[7] yield 48%.

^{1}H NMR (τ, C_6H_6): 6.7–8.1 (complex pattern, 3, $CH_3CH{=}CH_2$), 6.78 (s, 3, $CH_3CH{=}CH_2$), 8.7 (s, 15, C_5Me_5). $^{13}C\{^1H\}$ NMR (ppm from Me_4Si, C_6D_6): 12.5 (C_5Me_5), 29.5 ($CH_3CH{=}CH_2$), 74.6 ($CH_3CH{=}CH_2$), 82.2 ($CH_3CH{=}CH_2$), 117.9 (C_5Me_5).

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(15) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6529. (b) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *Ibid.* **1976**, *98*, 6529–6536.

(16) We originally postulated[7,8] that a proton is "removed more readily" from a tertiary carbon atom than from a secondary carbon atom, irrespective of the type of tantalacyclopentane complex. Clearly this is an oversimplification.

(17) Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6462–6463.

(18) Biefeld, C. G.; Eick, H. A.; Grubbs, R. H. *Inorg. Chem.* **1973**, *12*, 2166–2170.

(19) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellmann, J. D. *J. Am. Chem. Soc.* **1979**, *101*, 1593–1595.

(20) Krauss, H. L.; Stach, H. *Z. Anorg. Allg. Chem.* **1969**, *366*, 34–42.

(21) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238.

(22) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222.

TaCp″(cyclooctene)Br$_2$ was prepared from TaCp″(propylene)Br$_2$ (see chloro analogue[7]). ^{13}C{^{1}H} NMR (ppm from Me$_4$Si, C$_6$D$_6$): 12.5 ($\mathrm{C_5}\mathit{Me}_5$), 26.8, 36.1, 39.4 (aliphatic cyclooctene carbon atoms), 89.0 (olefinic cyclooctene carbon atoms), 118.1 ($\mathit{C}_5\mathrm{Me_5}$).

(2) Preparation of TaCp″(cyclooctene)(OMe)Cl. Solid NaOMe (0.22 g, 4 mmol) was added in small portions over a 2-h period to TaCp″(cyclooctene)Cl$_2$ (2.0 g, 4 mmol) partially dissolved in ethyl ether (80 mL). The mixture was stirred for 20 h and filtered. The ether was removed in vacuo, the red solid was extracted into pentane, and the mixture was filtered. The filtrate was concentrated in vacuo until red crystals began to form and then cooled to −30 °C. The red crystals were recrystallized from methylcyclohexane, yield 61%.

^{1}H NMR (τ, C$_6$H$_6$): 6.43 (s, CH$_3$O), 7.3–9.1 (complex pattern, cyclooctene), 8.32 (s, $\mathrm{C_5}\mathit{Me}_5$). ^{13}C NMR (ppm from Me$_4$Si, C$_6$D$_6$): 10.7 (q, $\mathrm{C_5}\mathit{Me}_5$, $^1J_{\mathrm{CH}} = 127$ Hz), 38.5, 37.5, 30.4, 30.3, 27.1 (2) (aliphatic cyclooctene carbon atoms), 61.2 (q, CH$_3$O, $^1J_{\mathrm{CH}} = 144$ Hz), 76.4, 67.3 (each a d, $^1J_{\mathrm{CH}} = 140$ Hz, olefinic carbon atoms), 114 (s, $\mathit{C}_5\mathrm{Me_5}$).

(3) Preparation of Cp″Cl(OMe)$\overline{\mathrm{TaCH_2CHMeCHMeCH_2}}$. TaCp″(cyclooctene)(OMe)Cl (1.08 g, 2 mmol) in 3 mL of pentane was treated with propylene (40 psi) until it all dissolved to give an orange solution (ca. 20 min). A crystalline sample of the tantalacycle was obtained by cooling the pentane solution to −30 °C, yield 0.24 g. The fact that the tantalacycle is so soluble prevented more efficient recovery. Two diastereomers of this *trans-β,β′*-dimethyltantalacycle are possible. They are found in about a 3:2 ratio and do *not* interconvert when the TaC$_4$ ring "pseudorotates" (see ref 7).

^{1}H NMR (τ, C$_6$D$_6$): 5.95 (s, both OMe groups), 6.75, 6.93, 8.13, 9.05, 9.65 (broad m, $\overline{\mathrm{TaCH_2CHMeCHMeCH_2}}$), 8.24, 8.25 (C$_5Me_5$ groups). ^{13}C{^{1}H} NMR (ppm from Me$_4$Si, toluene-d_8, −40 °C): 12.0 ($\mathrm{C_5}\mathit{Me}_5$ peaks overlap), ca. 26 (overlapping peaks, ring Me groups), 45.0, 45.8, 46.3, 47.9 ($\overline{\mathrm{TaCH_2}\mathit{C}\mathrm{HMe}\mathit{C}\mathrm{HMeCH_2}}$), 62.0, 62.6 (OMe groups), 77.2, 78.2, 81.3 (two overlapping) ($\overline{\mathrm{Ta}\mathit{C}\mathrm{H_2CHMeCHMe}\mathit{C}\mathrm{H_2}}$), 119.9 ($\mathit{C}_5\mathrm{Me_5}$ peaks overlap).

(4) Dimerization of Monoolefins by TaCp(CHCMe$_3$)Cl$_2$. In a typical reaction TaCp(CHCMe$_3$)Cl$_2$ (0.0690 g, 0.178 mmol) was dissolved in 8 mL of decane and placed in a pressure bottle with n-C$_8$H$_{18}$ internal standard. The red solution was warmed to 45.0 ± 0.5 °C in a constant-temperature bath and propylene was introduced (40 psi). Over a period of 15 min the solution changed from red to orange. Samples were removed by syringe through a septum inlet without releasing the pressure and quenched with air in small vials. (In a separate experiment it was shown that none of the dimers was formed when CpCl$_2\overline{\mathrm{TaCH_2CHMeCHMeCH_2}}$ was quenched with air.) GLC analysis showed 2,4,4-trimethyl-1-pentene; the yield increased to ~85% within 1 h and remained constant. The dimers of propylene (2,3-dimethyl-1-butene (92% relative yield), 2,3-dimethyl-2-butene (2%), and 2-methyl-1-pentene (6%)) were identified by GLC comparison with authentic samples on two GLC columns. The yield of dimers increased linearly with time for the first few hours of the reaction. Using the combined yields of the dimers at 0.5, 1, 2, and 4 h, and assuming that the dimerization is first order in tantalum, we calculated the rate constant to be 0.052 min^{-1} (45.0 °C). The rate of dimerization slowly decreased as a brown precipitate formed in the reaction mixture. After 24 h the supernatant above the brown precipitate was pale yellow; the dimerization had stopped after about 20 turnovers.

In a similar reaction under 4 psi of 1-butene there was no further change in the organic products after 17 h. They were identified by their GC/mass spectra as C$_8$H$_{16}$ (two peaks, 1.18 equiv/Ta) and C$_9$H$_{18}$ (0.59 equiv/Ta).

In a similar experiment employing 1-hexene an orange precipitate formed and the solution was colorless after 12 h. GLC analysis showed two peaks which are probably C$_{11}$H$_{22}$ products (0.56 equiv/Ta) and two peaks which are probably 1-hexene dimers (0.50 equiv/Ta).

(5) Dimerization of Monoolefins by CpCl$_2\overline{\mathrm{TaCH_2CH_2CH_2CH_2}}$. (a) Ethylene. A solution of CpCl$_2\overline{\mathrm{TaCH_2CH_2CH_2CH_2}}$ (0.07 g, 0.2 mmol) and n-C$_8$H$_{18}$ internal standard in 10 mL of mesitylene was stirred under 40 psi of ethylene at 80 °C. After 2 h the solution was cooled to 0 °C and sampled with a cold syringe. GLC analysis showed 1-butene (9.5 equiv/Ta), *trans*-2-butene (0.30 equiv/Ta), and *cis*-2-butene (0.031 equiv/Ta). All three products were identified by comparison with authentic samples on two columns. There were also two major higher boiling products that were both identified as C$_6$H$_{12}$ by their GC/mass spectra (combined yield 0.42 equiv/Ta). After 15 h the yields were 22 (1-butene), 0.76 (*trans*-2-butene), 0.11 (*cis*-2-butene), and 5.2 equiv/Ta (C$_6$H$_{12}$).

(b) Ethylene and Propylene Codimerization. A solution of CpCl$_2\overline{\mathrm{TaCH_2CH_2CH_2CH_2}}$ (0.077 g, 0.206 mmol) and C$_7$H$_{16}$ internal standard was stirred under 20 psi of ethylene in a 100-mL pressure bottle for 15 min. The gas line was changed to propylene and the solution was stirred under 50 psi of propylene for 15 min. The gas inlet to the bomb was closed and samples were withdrawn by syringe through a septum without releasing the pressure. After 3 h at 25 °C, GLC analysis showed no volatile products. The solution was heated to 70 °C for 12 h and GLC analysis showed three major products. Two of them were identified as 1-butene (16.4 equiv/Ta) and 2,3-dimethyl-1-butene (0.53 equiv/Ta) by their retention times. A third product had an intermediate retention time and was assumed to be a C$_5$H$_{10}$ ethylene/propylene codimer (5.6 equiv/Ta).

(6) Dimerization of Propylene by TaCp(CHCMe$_3$)Br$_2$. The same procedure was used as with the TaCp(CHCMe$_3$)Cl$_2$ catalyst. The 2,4,4-trimethyl-1-pentene formed more slowly and reached a stable maximum of 65% after 4 h. The dimer products were 2,3-dimethyl-1-butene (89%, relative yield), 2,3-dimethyl-2-butene (3%), and 2-methyl-1-pentene (8%). The rate of dimerization slowly decreased and the final number of turnovers after 21 h was 40. It was difficult to get a rate constant for dimerization to compare with the TaCp(CHCMe$_3$)Cl$_2$ system since the active catalyst was formed slowly and the yield of dimers did not increase linearly with time. It was estimated that the bromide catalyst is 2.5 times faster than the chloride catalyst.

(7) Dimerization of Propylene by TaCp″(propylene)Cl$_2$. In a typical experiment TaCp″(propylene)Cl$_2$ (0.0523 g, 0.122 mmol) was dissolved in 6.1 mL of decane with n-octane internal standard (0.1738 g, 1.205 mmol). The purple solution was stirred under 40 psi of propylene in a glass pressure bottle at 45.0 °C, and within several minutes the color changed to light orange. Samples were removed by syringe and quenched with dry O$_2$ in small vials. GLC analysis showed two dimers of propylene (relative yields): 2,3-dimethyl-1-butene (98.2%) and 2-methyl-1-pentene (1.8%). They were identified by GLC comparison with authentic samples on two columns. The initial rate constant of dimerization was 0.044 ± 0.007 min^{-1}, and the total number of turnovers before catalyst deactivation (~24 h) was 22. The product distribution and rate did not change significantly in ether ($k = 0.041$ min^{-1}). The presence of excess propylene dimers (9 equiv/Ta of 2,3-dimethyl-1-butene and 9 equiv/Ta of 2,3-dimethyl-2-butene) did not affect the initial rate of dimerization ($k = 0.050$ min^{-1}).

At 70 °C in decane the initial rate constant for dimerization was 0.27 min^{-1}, and the total number of turnovers before catalyst deactivation (27 h) was 155. A reaction done under the same conditions with twice as much catalyst and solvent gave $k = 0.34$ min^{-1} and 497 turnovers.

(8) Activation Parameters for Propylene Dimerization by TaCp″(propylene)Cl$_2$. The same procedure was used for each dimerization. In a typical example, a weighed sample of TaCp″(propylene)Cl$_2$ (0.1561 g, 0.3637 mmol) and n-heptane internal standard (50 μL, 0.0340 g, 0.3393 mmol) were added to a 25-mL glass pressure bottle, and the stainless steel head was attached. The apparatus was connected to a propylene supply and enough toluene (5.2 mL) was added to make a 0.07 M solution of the catalyst. The bottle was pressurized to 40 psi with propylene and then placed in a constant-temperature bath. The solution was stirred magnetically. After 15 min was allowed for thermal equilibration, samples were withdrawn about every 15 min by syringe and quenched with dry O$_2$ in small, septum-capped vials. The rate of dimer formation was constant during the sampling period of 60–90 min. Each rate constant k was calculated by a linear least-squares fit of the dimer yield vs. time: $4.7 \pm 0.6 \times 10^{-4}$ (0.0 °C), $1.60 \pm 0.20 \times 10^{-2}$ (31.5 °C), $8.7 \pm 0.9 \times 10^{-2}$ (50.0 °C), $4.2 \pm 0.4 \times 10^{-1}$ (70.0 °C), and 1.61 ± 0.20 min^{-1} (90.0 °C). The least-squares correlation coefficient (r^2) for the data from the 0 °C reaction was 0.90; all others were ≥0.99. The errors in k are estimated values. Using these six values of k and temperature, a least-squares fit of $\ln \{kh/\mathbf{k}T\}$ vs. $1/T$ (K) gave $\Delta H^{\ddagger} = 17.2 \pm 0.6$ kcal mol^{-1} (17.22 exact), $\Delta S^{\ddagger} = -18 \pm 2$ eu (−18.5 exact), and $\Delta G^{\ddagger}$(25 °C) $= 22.7 \pm 1.2$ kcal mol^{-1} (Figure 1). The error in any activation parameter was calculated by normal statistical methods and represents two standard deviations.

(9) Isolation and Characterization of the 1-Pentene Dimers. The volatile products of the dimerization of 25 equiv of 1-pentene by TaCp″(styrene)Cl$_2$ in C$_6$D$_6$ (60 °C) were isolated by a high-vacuum bulb-to-bulb distillation and identified as 2-propyl-3-methyl-1-hexene (87%) and 2-propyl-1-heptene (13%) by comparison with authentic samples by GLC coinjection, ^{1}H NMR, and ^{13}C NMR.

2-Propyl-3-methyl-1-hexene was prepared in 29% yield by a standard Wittig reaction[23] from commercially available 5-methyl-4-octanone (Chemical Samples Co.). ^{1}H NMR (C$_6$D$_6$): 5.27 (m, 2, =CH$_2$), 7.40–9.30 with largest peaks at 8.95, 9.06, and 9.10 (m, 18, aliphatic

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[23] Wittig, G.; Schoellkopf, U. "Organic Syntheses", Collect. Vol. V; Wiley: New York, 1973; pp 751–754.

protons). ^{13}C NMR ($CDCl_3$, 67.89 MHz, ^{1}H gated decoupled; see Figure 2 for peak assignments): 13.9 (q, 1 or 2), 14.1 (q, 1 or 2), 20.1 (q, 3), 20.6 (t, 4), 21.3 (t, 5), 36.1 (t, 6), 38.2 (t, 7), 39.8 (d, 8), 107.3 (t, 9), 154.5 ppm (s, 10). Peak assignments were made on the basis of multiplicities in the ^{1}H gated decoupled spectrum, and chemical shifts (using additivity rules[24] and ^{13}C NMR shifts of model compounds).

2-Propyl-1-heptene was prepared in 59% yield by a standard Wittig reaction from commerically available 4-nonanone (Chemical Samples Co.). ^{1}H NMR (C_6D_6): 5.23 (m, 2, $=CH_2$), 7.40–9.40 with the largest peaks at 8.71, 8.78, and 9.01 ppm (m, 18, aliphatic protons). ^{13}C NMR ($CDCl_3$, 67.89 MHz, ^{1}H gated decoupled; see Figure 2 for peak assignments): 13.8 (q, 1 or 2), 14.0 (q, 1 or 2), 21.0 (t, 3), 22.7 (t, 4), 27.7 (t, 5), 31.8 (t, 6), 36.1 (t, 7), 38.4 (t, 8), 108.6 (t, 9), 149.9 ppm (s, 10). Peak assignments were made on the basis of multiplicities in the ^{1}H gated decoupled spectrum, and chemical shifts (using additivity rules[24] and ^{13}C NMR shifts of model compounds).

(10) Isolation and Characterization of the 1-Octene Dimers. A solution of TaCp″(cyclooctene)Cl_2 (0.10 g) in 1-octene (5.0 g, 45 mmol) was heated to ~60 °C for 5 h. GLC analysis showed that 83% of the 1-octene had been converted to two dimers in the ratio 82:18. The reaction mixture was passed down a short column of alumina, and the products were isolated by preparative GLC.

Major product (2-(*n*-hexyl)-3-methyl-1-nonene): ^{1}H NMR ($CDCl_3$) 5.37 (m, 2, $=CH_2$), 7.40–9.74 with large peaks at 8.77, 8.98, 9.10, 9.13 ppm (m, 30, aliphatic protons); ^{13}C NMR ($CDCl_3$, 67.89 MHz, ^{1}H gated decoupled) 14.1 (q, $^1J_{CH}$ = 126 Hz), 20.2 (q, $^1J_{CH}$ = 127 Hz), 22.7 (t, $^1J_{CH}$ = 125 Hz), 27.5 (t, $^1J_{CH}$ = 126 Hz), 28.2 (t, $^1J_{CH}$ = 126 Hz), 29.3 (t, $^1J_{CH}$ = 126 Hz), 29.5 (t, $^1J_{CH}$ = 126 Hz), 31.9 (t, $^1J_{CH}$ = 131 Hz), 33.9 (t, $^1J_{CH}$ = 130 Hz), 35.8 (t, $^1J_{CH}$ = 128 Hz), 40.0 (d, $^1J_{CH}$ = 132 Hz), 107.1 (t, $=CH_2$, $^1J_{CH}$ = 153 Hz), 155.1 ppm (s, $C{=}CH_2$); mass spectrum *m/e* (rel intensity) 224 (4.2, $C_{16}H_{32}$, parent ion), 140 (54.5), 111 (93.7), 83 (65.9), 71 (58.2), 70 (100), 69 (100), 55 (100).

Minor product (2-(*n*-hexyl)-1-decene): ^{1}H NMR ($CDCl_3$) 5.27 (m, 2, $=CH_2$), 7.78–9.43 with large peaks at 7.97, 8.68, 9.10 ppm (m, 30, aliphatic protons); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.89 MHz) 14.1, 22.7, 27.8, 29.1, 29.3, 31.8, 31.9, 36.1, 108.3 ppm; the signal to noise ratio was low owing to the small sample size; mass spectrum *m/e* (rel intensity) 224 (12.1, $C_{16}H_{32}$, parent ion), 139 (15.8), 126 (16.3), 111 (50.4), 56 (100).

(11) Isolation and Characterization of the 4-Methyl-1-pentene Dimers. 4-Methyl-1-pentene (3.50 g, 41.6 mmol) was added to a solution of TaCp″(propylene)Cl_2 (0.10 g, 0.23 mmol) in 6 mL of benzene. The orange solution was heated to 50 °C and after 44 h the color had changed to dark red. GLC analysis showed that 99% of the 4-methyl-1-pentene had been converted into two new products in the ratio 61:39. The reaction mixture was passed down a short column of alumina to remove Ta compounds, and the products were isolated by preparative GLC.

Major product (2-isobutyl-3,5-dimethyl-1-hexene): ^{1}H NMR ($CDCl_3$) 5.28, 5.35 (m, m, 2, $=CH_2$), 7.58–9.45 with large peaks at 8.18, 8.98, 9.08, and 9.18 ppm (m, 22, aliphatic protons); ^{13}C NMR ($CDCl_3$, 67.89 MHz, ^{1}H gated decoupled) 20.4 (q, $^1J_{CH}$ = 128 Hz), 22.7 (q, $^1J_{CH}$ = 126 Hz), 23.0 (q, $^1J_{CH}$ = 125 Hz), 25.6 (d, $^1J_{CH}$ = 127 Hz), 26.3 (d, $^1J_{CH}$ = 126 Hz), 37.1 (d, $^1J_{CH}$ = 127 Hz), 44.2 (t, $^1J_{CH}$ = 127 Hz), 45.6 (t, $^1J_{CH}$ = 126 Hz), 108.3 (t, $C{=}CH_2$, $^1J_{CH}$ = 154 Hz), 154.2 ppm (s, $C{=}CH_2$); mass spectrum *m/e* (rel intensity) 112 (82.1, C_4H_8, parent ion), 83 (50.0), 70 (100).

Minor product (2-isobutyl-6-methyl-1-heptene): ^{1}H NMR ($CDCl_3$) 5.33 (m, 2, $=CH_2$), 7.83–9.56 with large peaks at 8.13, 9.03, 9.17 ppm (m, 22, aliphatic protons); ^{13}C NMR ($CDCl_3$, 67.89 MHz, ^{1}H gated decoupled) 22.6 (q, $^1J_{CH}$ = 126 Hz), 25.6 (t, $^1J_{CH}$ = 123 Hz), 26.1 (d, $^1J_{CH}$ = 123 Hz), 28.0 (d, $^1J_{CH}$ = 125 Hz), 36.0 (t, $^1J_{CH}$ = 125 Hz), 38.8 (t, $^1J_{CH}$ = 123 Hz), 46.0 (t, $^1J_{CH}$ = 126 Hz), 109.9 (t, $C{=}CH_2$, $^1J_{CH}$ = 158 Hz), 149.5 ppm (s, $C{=}CH_2$); mass spectrum *m/e* (rel intensity) 168 (14.9, $C_{12}H_{24}$, parent ion), 83 (68.1), 70 (53.9), 69 (57.4), 56 (100).

(12) Isolation and Characterization of the 4,4-Dimethyl-1-pentene Dimer. A ^{13}C NMR sample of TaCp″($Me_3CCH_2CH{=}CH_2$)Cl_2 with 4 equiv of $Me_3CCH_2CH{=}CH_2$ was stored at 25 °C for 1 week until all of the excess olefin had been dimerized. The volatile products were isolated by a high-vacuum bulb-to-bulb distillation. GLC analysis showed a single product. It was isolated by preparative GLC. ^{1}H NMR ($CDCl_3$): 5.17, 5.32 (m, m, 2, $=CH_2$), 7.80–9.27 (m, CH_2), 9.07, 9.10 ppm (s, s, CMe_3), total area of aliphatic protons = 26. ^{13}C NMR (toluene-d_8, 67.89 MHz, ^{1}H gated decoupled): 23.6 (t, $^1J_{CH}$ = 119 Hz), 29.7 (q, $^1J_{CH}$ = 126 Hz), 30.3 (q, $^1J_{CH}$ = 124 Hz), 30.4, 31.6 (s), 39.2 (t, $^1J_{CH}$ = 125 Hz), 44.3 (t, $^1J_{CH}$ = 123 Hz), 50.0 (t, $^1J_{CH}$ = 128 Hz), 112.8 (t, $C{=}CH_2$, $^1J_{CH}$ = 154 Hz), 148.1 ppm (s, $C{=}CH_2$). The signal to noise ratio in the ^{1}H decoupled ^{13}C NMR spectrum was very high. As little as 4% of another isomer could have been observed. Mass spectrum *m/e* (rel intensity): 196 (20.5, $C_{14}H_{28}$, parent ion), 140 (15.2), 112 (30.2), 111 (16.8), 57 (100, CMe_3). All of the data are consistent with this compound being 2-neopentyl-6,6-dimethyl-1-heptene.

(13) Effect of Catalyst and Olefin Concentrations on the Dimerization Rate of 1-Octene. The procedure was identical with the procedure used for the dimerization of 1-octene in the comparative rate study (see below). The concentrations of 1-octene and Ta catalyst were varied systematically. If the rate equation is assumed to be d(dimers)/dt = k[Ta], then the integrated form is [(dimers)$_t$ − (dimers)$_0$]/[Ta] = kt. Values of k were determined by a linear least-squares fit of the yield of dimers vs. time. In each case the correlation coefficient (r^2) was >0.99. The results are listed in Table II.

(14) Dimerization of α-Olefins by TaCp″(cyclooctene)Cl_2. Comparative Rates and Product Distribution. Each dimerization was done at 50.0 ± 0.5 °C in a solution of the olefin and toluene. The initial concentration of TaCp″(cyclooctene)Cl_2 was 0.07 M. In all the dimerizations except of ethylene and propylene (each 40 psi), the olefin concentration was 2.8 M. *n*-Alkanes were used as internal standards. The catalyst and internal standard were transferred to the reaction flask inside a drybox. The toluene and olefin (in that order) were added by syringe through a septum inlet, and the solutions were thermally equilibrated for 15 min before sampling. During the first hour of each reaction, five samples were removed by syringe for GLC analysis. They were quenched with dry O_2 in septum-capped vials. The relative GLC response of 1-butene vs. an internal standard was assumed to be the ratio of their molecular weights. All other GLC response factors were determined experimentally by using authentic samples or pure isolated samples. The product distributions are given in Table I; see the preceding sections of the Experimental Section for product identification. Each rate constant was calculated by a linear least-squares fit of the data to the integrated rate equation (see preceding section). Errors in k are estimated values. Correlation coefficients (r^2) were all >0.99.

Because of the difficulty of quantitatively transferring 1-butene, the ethylene dimerization reaction was only sampled once. After 60 min the reaction mixture was rapidly cooled to 0 °C. A sample was withdrawn into a cold syringe and quenched with dry O_2 in a precooled septum-capped vial; k = 0.021 ± 0.002 min^{-1}.

The propylene reaction was done in a 25-mL glass pressure bottle under 40 psi of propylene; k = 0.087 ± 0.009 min^{-1}.

1-Pentene was dimerized in a 25-mL glass pressure bottle under 40 psi of nitrogen in order to keep the 1-pentene in solution at 50 °C.

1-Octene, 4-methyl-1-pentene, and 4,4-dimethyl-1-pentene were dimerized in a 25-mL round-bottom flask equipped with a Teflon stopcock with a septum inlet. The reaction was connected to a N_2 line by a syringe needle through the septum inlet. The Teflon stopcock was opened only for sampling.

(15) Preparative Scale Dimerization of 1-Octene. 1-Octene was dried over activated 4 Å molecular sieves for 24 h and degassed by three freeze–pump–thaw cycles on a high-vacuum line. TaCp″(propylene)Cl_2 (0.1145 g, 0.2668 mmol) was transferred to a 250-mL round-bottom flask equipped with a vacuum stopcock inlet. The flask was evacuated and cooled with liquid N_2. 1-Octene (77.7 g, 0.692 mmol) was distilled into the cold flask in vacuo. The light orange solution of 1-octene and catalyst was heated to 100 °C. After 20 h the dark orange color of the solution indicated that the dimerization was complete. The solution was passed down a short column of alumina to remove Ta compounds and distilled at 11 mm to give 75.3 g of dimers (97%, bp 148–155 °C). GLC analysis showed that the two major dimer products (in a ratio of 78:22) account for >97% of the volatile products.

(16) Preparation of 2-Deuterio-1-pentene. An oven-dried 250-mL two-neck round-bottom flask was charged with 1.96 g (80.5 mmol) of Mg and connected to a small addition funnel and a distillation apparatus. The entire apparatus was flushed with N_2, and 20 mL of dry THF was added to the flask. 2-Bromo-1-pentene (12.0 g, 80.5 mmol) was dissolved in 20 mL of THF and added dropwise to the magnesium suspension from the addition funnel. After ~20% of the 2-bromo-1-pentene had been added, the mixture was heated until the Grignard reaction initiated and caused the THF to boil vigorously. The heating was stopped and 20 mL of THF was added to the mixture. The 2-bromo-1-pentene addition was continued at a rate which maintained a gentle reflux of the THF. At the end of the addition, the mixture was heated to reflux for an additional 20 min. THF (20 mL) was distilled out of the reaction mixture to remove any 1-pentene-d_0 that may have been formed. The solution was cooled to 0 °C and 2.9 mL of D_2O was slowly added to the Grignard solution through a septum inlet with an oven-dried 5-mL syringe which had been cooled in a stream of dry N_2 and rinsed with fresh D_2O (99.7% D) four times. The product was distilled out of the reaction mixture until the stillhead temperature was 66 °C (~bp of THF). A second distillation on a spinning band column gave 4.43 g (77%) of pure 2-deuterio-1-pentene: mass spectrum *m/e* (intensity) 73 (0.1), 72 (5.4), 71 (100.0,

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(24) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: Philadelphia, 1976.

C_5H_9D), 70 (<0.1), 69 (0.8), 68 (3.9), 67 (1.5). Comparison to a mass spectrum of 1-pentene-d_0 showed that the product was ≥99.5% d_1.

(17) Dimerization of 2-Deuterio-1-pentene. The procedure was identical with the dimerization of 1-pentene in the comparative rate study; $k = 0.030 \pm 0.003$ min^{-1}. The individual rate constants are 0.022 ± 0.002 (tt dimer) and 0.0085 ± 0.0008 min^{-1} (ht dimer). For undeuterated 1-pentene they are 0.073 ± 0.007 and 0.010 ± 0.00) min^{-1}, respectively. Therefore, for 2-propyl-3-methyl-1-hexene $k_H/k_D = 3.34 \pm 0.67$ and for 2-propyl-1-heptene $k_H/k_D = 1.20 \pm 0.24$.

After 10 h GLC analysis showed that the dimerization was 80% complete. The reaction mixture was passed down a short column of alumina, and the dimers were isolated by preparative GLC.

(a) 2-Propyl-3-deuterio-3-(monodeuteriomethyl)-1-hexene (tt Dimer). ^{1}H NMR ($CDCl_3$): 5.27 (m, 2, $=CH_2$), 7.50–9.63 ppm (m, 16, aliphatic protons). ^{2}H{^{1}H} NMR ($CDCl_3$, ppm upfield of $CDCl_3$): 5.16 (s, 1), 6.25 (s, 1). ^{13}C{^{1}H} NMR ($CDCl_3$, 67.89 MHz): identical with the spectrum of the undeuterated compound except that the singlet at 20.1 ppm is replaced by a triplet at 19.7 ppm ($^1J_{CD}$ = 18.8 Hz), and the singlet at 39.8 ppm is replaced by a triplet at 39.2 ppm ($^1J_{CD}$ = 19.6 Hz). See the preparation of the authentic undeuterated compound and Figure 3 for peak assignments. We estimate from the ^{13}C NMR data that in this sample we could have detected as little as 10% of 2-propyl-3-methyl-1-hexene which was not deuterated in the specified positions.

(b) 2-Propyl-3,4-dideuterio-1-heptene (ht Dimer). ^{1}H NMR ($CDCl_3$): 5.30 (m, 2, $=CH_2$), 7.80–9.50 (m, 16, aliphatic protons). ^{2}H{^{1}H} NMR ($CDCl_3$, ppm upfield of $CDCl_3$): 5.27 (s, 1), 5.83 (s, 1). ^{13}C{^{1}H} NMR ($CDCl_3$): identical with spectrum of the undeuterated compound except that the singlet at 27.7 ppm is replaced by a triplet at 27.2 ppm ($^1J_{CD}$ = 19.3 Hz) and the singlet at 36.1 ppm is replaced by a triplet at 35.7 ppm ($^1J_{CD}$ = 19.1 Hz). See the preparation of the authentic undeuterated compound and Figure 2 for peak assignments. We estimate from the ^{13}C NMR data that in this sample we could have detected as little as 10% of 2-propyl-1-heptene which was not deuterated in the specified positions.

(18) Codimerization of Propylene and 2-Deuterio-1-pentene. (a) Preparation of Authentic Codimers. TaCp″(cyclooctene)Cl_2 (0.159 g, 0.32 mmol) was suspended in 4 mL of pentane into a glass pressure bottle and stirred under 40 psi propylene at 50 °C until a yellow-orange solution formed. Then 1 mL of 1-pentene was added by syringe, followed by another after 5 h. Samples for GLC analysis were withdrawn within the first hour. For 2-isopropyl-1-pentene (isomer A, Figure 4), $k_H(A) = 4.1$ and 4.2 in two different runs; for 2,3-dimethyl-1-hexene (isomer B, Figure 4), $k_H(B) = 2.0$ and 2.3 in two different runs. After 28 h the solution was passed down a short column filled with alumina and distilled by using a short Vigreux column to eliminate most of the solvent and 2,3-dimethyl-1-butene. The mixture of the two major C_8 codimers was isolated by preparative GLC and examined by ^{13}C NMR; chemical shifts and assignments are shown in Figure 4. Authentic samples were prepared by a Wittig reaction from the two commercially available ketones. They were identical in all respects with the products of the catalytic reaction. (The units of k are 10^{-2} min^{-1}.)

(b) Preparation of Labeled Codimers. Catalytic reactions identical with the above using 2-deuterio-1-pentene gave A and B with $k_D(A) =$ 4.2 and 3.9 and $k_D(B) = 0.66$ and 0.70. Therefore $k_H/k_D = 1.0$ for A and $k_H/k_D = 3.2$ for B. The mixture of A and B was isolated by preparative GLC and examined by ^{13}C NMR at 67.89 MHz (Figure 4). Approximately 5% of authentic all-protio A (prepared from the ketone) was added to confirm that the peak at δ 33.843 was due to the A4 carbon atom with a proton attached. By comparing the two peak areas we could show that the codimer A was labeled to the extent of 97–98% as shown. (The units of k are 10^{-2} min^{-1}.)

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Steric Effects. A Study of a Rationally Designed System

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Abstract: The principles for the rational design of systems suitable for the study of steric effects are defined. A suitable *molecular framework* [6-(2-X-phenyl)-5-Y-1,1-dimethylindan, **1**] was synthesized and a study of internal rotation by dynamic NMR spectroscopy (DNMR) of 33 derivatives, differing principally in the nature of the *molecular fragment* (X), showed the following. (i) For **1** (Y = Me; X = halogen) the rotational barriers ($\Delta G^{\ddagger}$) increase smoothly and monotonically with the van der Waals radius of X (r_x), which permits the estimation of *effective* r_x for fragments of lower symmetry. (ii) The rotational barriers are the sum of additive contributions, designated *interference values* (I^{H-X}), which can be used to predict the rotational barriers in 2,2′-disubstituted biphenyls. (iii) A simple geometrical parameter, apparent overlap (r^*), which is related to the distortion of the framework in the transition state, is proposed and found to have an excellent linear correlation with the barrier to rotation in 2,2′-disubstituted biphenyls. (iv) This correlation can be used for a semiquantitative estimation of rotational barriers in biaryls and other systems.

Steric hindrance can be defined as the energy penalty associated with crowding of nonbonded molecular fragments. The study of this phenomenon must therefore involve notions of size (typically defined in terms of van der Waals radii[1]) of the fragments, the geometry of the systems within which they interact, and the energy associated with the interaction(s). Steric hindrance forms a persistent theme in chemistry and has been invoked to rationalize innumerable observations. It is amenable to theoretical treatments,[2] but *systematic* experimental studies are relatively few with most of the recent work being summarized by Charton,[3] who has established statistically significant correlations between the size of molecular fragments and the energetics of a number of processes reported by other workers. Steric interactions have also been recently critically reviewed by Förster and Vögtle.[4]

We decided to approach the problem by designing a system whose energetics would shed light on the relationship between the

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