

TANTALACYCLOPENTANE COMPLEXES AND THEIR ROLE IN THE CATALYTIC DIMERIZATION OF OLEFINS

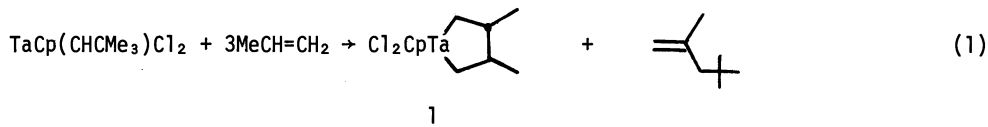
Richard Schrock*, Stephan McLain, and José Sancho

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

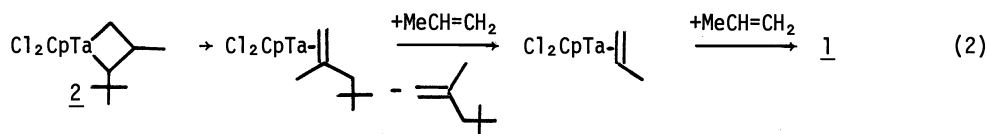
Abstract - β, β' -Disubstituted and α, β' -disubstituted tantalacyclopentane complexes are intermediates in the selective catalytic dimerization of $RCH=CH_2$ ($R = Me, Pr, CH_2CHMe_2, CH_2CMe_3$) to a mixture of the tail-to-tail and the head-to-tail dimers, respectively. Deuterium labelling studies show that neither dimer forms by reductive elimination from an alkenyl hydride intermediate directly. The most satisfactory explanation is that the tantalum hydride adds back to the alkenyl double bond to give a tantalacyclobutane complex which then rearranges to the olefin. The fact that formation of the metallacyclobutane ring is probably a relatively slow step of the reaction can explain why the type of dimer changes from nearly exclusively the tt-dimer when $R = Me$ to exclusively the ht-dimer when $R = CH_2CMe_3$.

INTRODUCTION

Tantalacyclopentane complexes were first discovered as products of the reaction of $TaCp(CHCMe_3)Cl_2$ ($Cp = \eta^5-C_5H_5$) with olefins (Ref. 1). An example is shown in equation 1.



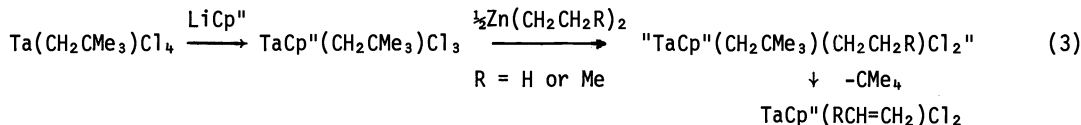
The intermediate in this reaction is believed to be a tantalacyclobutane complex (2; equation 2) which rearranges selectively to a 2,4,4-trimethyl-1-pentene complex. 2,4,4-Trimethyl-1-



pentene must be displaced by propylene to give a propylene complex which then reacts with another equivalent of propylene to give 1. Excess propylene is dimerized primarily to 2,3-dimethyl-1-butene by 1 but the catalytic activity is relatively short-lived (ca. 20 turnovers). We have since found that the analogous $\eta^5-C_5Me_5$ system ($Cp'' = \eta^5-C_5Me_5$) is well-behaved and amenable to more detailed study.

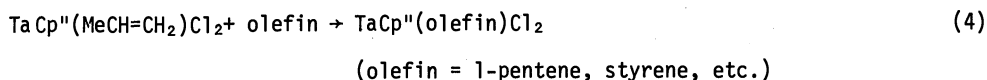
RESULTS AND DISCUSSION

An ethylene or propylene complex analogous to that shown in equation 2 can be prepared as shown in equation 3 (Ref. 2). The propylene complex is especially useful for preparing other



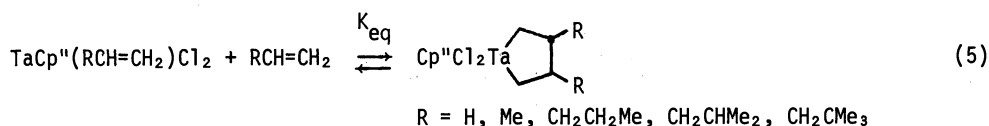
* Author to whom correspondence should be sent.

representative olefin complexes (olefin = 1-pentene, styrene, neopentylethylene, cis-2-pentene, or cyclooctene) by what we can for now simply call a displacement reaction (equation 4). (The reaction actually involves the formation and decomposition of metallacyclopentane




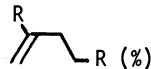
complexes, as well as simple displacement (Ref. 2.) Two olefin complexes which cannot be prepared are a trans-2-pentene complex and an isobutylene complex, presumably for steric reasons. In the former case ca. 20% of the 1-pentene complex was the only isolable species.

Orange metallacyclopentane complexes form when $\text{RCH}=\text{CH}_2$ is added to purple to red $\text{TaCp}''(\text{RCH}=\text{CH}_2)\text{Cl}_2$, except when $\text{R} = \text{Ph}$ (probably for electronic reasons). Metallacyclopentane complexes do not form from internal olefins. All metallacycles are trans- β,β' -disubstituted as shown by low temperature ^{13}C NMR experiments; two C_α carbon signals are seen and both are triplets in the gated decoupled spectrum. These metallacycles readily lose $\text{RCH}=\text{CH}_2$ to give back the olefin complex (equation 5). When $\text{R} = \text{H}$ or Me K_{eq} is large, but when $\text{R} = \text{CH}_2\text{CMe}_3$ $K_{\text{eq}} \approx 1$ at 0°C ; the metallacycle, in fact, cannot be observed at room temperature in the latter case.

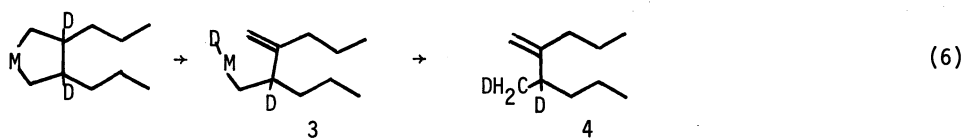


We have shown that a β,β' -disubstituted metallacyclopentane complex decomposes to give the tail-to-tail (tt) dimer, the 2,3-disubstituted-1-butene (Ref. 2). In the presence of excess olefin not only the tt-dimer but the ht-dimer forms catalytically in a ratio and at a rate which depend on the size of R (Table 1; Ref. 3). We studied the mechanism of this dimeriza-

TABLE 1. Five Catalytic Dimerizations at 50°C in Toluene

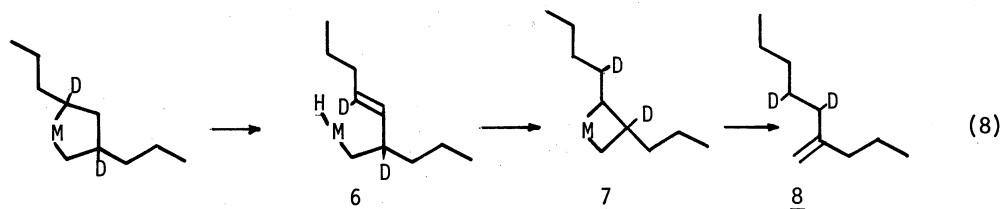
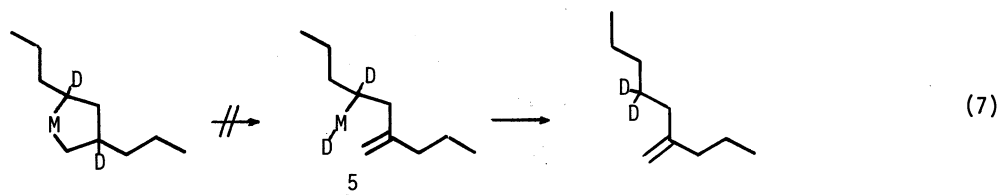
Olefin	 (%)	 (%)	$k_{\text{obs}}(\text{min}^{-1}) \times 10^2$
$\text{CH}_2=\text{CH}_2$	— 100% 1-butene —	—	2 ± 1
$\text{CH}_2=\text{CHMe}$	98	2	9.4 ± 0.9
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{Me}$	88	12	8.3 ± 0.8
$\text{CH}_2=\text{CHCH}_2\text{CHMe}_2$	61	39	4.9 ± 0.5
$\text{CH}_2=\text{CHCH}_2\text{CMe}_3$	0	100	2.6 ± 0.3

tion using 2-deutero-1-pentene. The tt-dimer was formed more slowly than that with unlabeled 1-pentene ($k_{\text{H}}/k_{\text{D}} = 3.3 \pm 0.6$) and was shown to be $> 90\%$ 4 by ^{13}C NMR (equation 6).

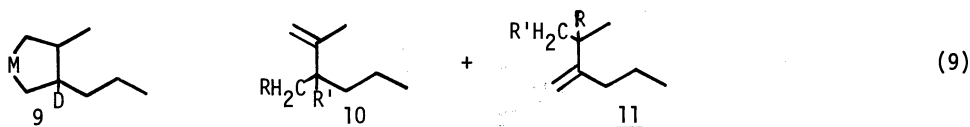


This result is consistent with formation of a butenyl hydride intermediate 3 followed by reductive elimination of the observed product (4). But the ht-dimer is not that expected by reductive elimination from one of the two possible intermediate butenyl hydrides (5; equation 7). The product is, instead, 8 (equation 8). Note that the isotope effect is small ($k_{\text{H}}/k_{\text{D}} = 1.2 \pm 0.2$). The most plausible explanation is that 6 forms and collapses to 7, the type of metallacyclobutane complex which we have invoked to explain how (e.g.) propylene reacts with $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)\text{Cl}_2$ (Ref. 1); in this case it rearranges exclusively to give the type of product shown. Unfortunately, we cannot tell from this data alone if 3 also contracts to an MC_3 (metallacyclobutane) complex since the position of the deuterium atoms in the product would be the same. Therefore we designed an experiment to answer this question.

Codimerization of propylene and 2-deutero-1-pentene yields (in addition to propylene and 2-deutero-1-pentene dimers) four co-dimers, two of which (10 and 11, equation 9) come from 9

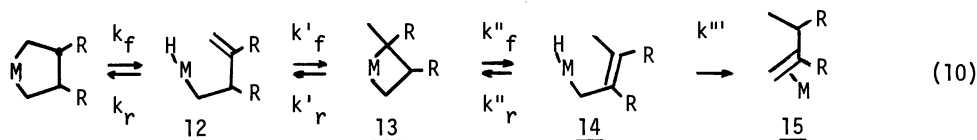


and therefore predominate (ca. 80% of the co-dimer mixture). ^{13}C NMR spectra show that they are the ones expected from the ring contraction pathway ($\text{R}' = \text{H}$, $\text{R} = \text{D}$; equation 9),

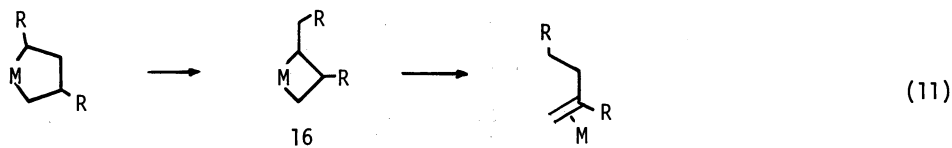


not those expected from the reductive elimination pathway ($\text{R}' = \text{D}$, $\text{R} = \text{H}$). Note that, as expected, $k_{\text{H}}/k_{\text{D}}$ for forming 10 is ca. 3.5 while that for forming 11 is ca. 1.2. Therefore we conclude that the β,β' -substituted metallacyclopentane complexes, $(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\text{TaCH}_2\text{CHRCHRCH}_2$, also decompose by forming a metallacyclobutane intermediate which then rearranges selectively to one of two possible olefins.

Let's look at the decomposition of one of the metallacycles in more detail (equation 10).

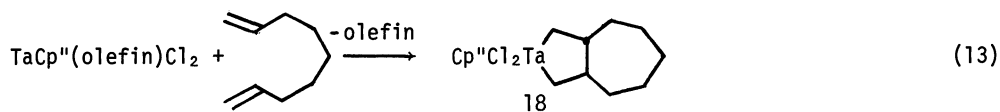
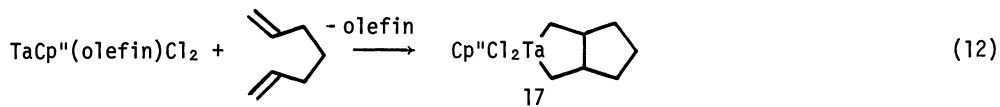


It seems reasonable to propose that metallacyclobutane complexes such as 13 decompose rapidly ($k''_{\text{f}} > k'_{\text{r}}$) since we have never seen any evidence for them (in NMR spectra, for example) when we prepare them by adding olefins to $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ (Ref. 1). We also propose that k''' is large relative to k''_{r} . This might seem problematic since we have just found that k for reductive elimination from 12 is slow relative to k'_{f} or k_{r} . It is therefore more consistent to view 15 as forming when M-H adds to the double bond in 14. We must now consider the first two steps. If $k'_{\text{f}} \gg k_{\text{r}}$ then the overall rate is proportional to k_{f} . If $k'_{\text{f}} \ll k_{\text{r}}$ then the overall rate is proportional to Kk'_{f} (where $K = k_{\text{f}}/k_{\text{r}}$). We believe the latter is more plausible, i.e., it should be more difficult to form an MC_3 ring than an MC_4 ring. This conclusion can help explain the switchover from *tt*-dimer to *ht*-dimer; the MC_3 species which must form (16 in equation 11) should do so more easily as R becomes larger relative to the rate at



which 13 (a more crowded species) forms.

It is interesting in this light to speculate why a complex such as 17 (equation 12) is so stable thermally (cf. Ref. 4) while 18 (equation 13) is no more stable than the metallacycle made with propylene. (Note that 17 is virtually all *cis* and 18 all *trans* about the ring



junction (Ref. 5)). Either K or k'_f (or both) for 17 is(are) significantly smaller than K or k'_f for 18. Since the intermediate metallacyclobutane complex formed from 17 should be considerably more strained than that formed from 18, k'_f for 17 should be smaller (perhaps significantly so) than that for 18. We cannot say at this time whether K for 17 is also smaller than K for 18.

REFERENCES

1. S.J. McLain and R.R. Schrock, *J. Am. Chem. Soc.*, **99**, 3519-3520 (1977).
2. S.J. McLain, C.D. Wood, and R.R. Schrock, *J. Am. Chem. Soc.*, **101**, 4558-4570 (1979).
3. S.J. McLain, J. Sancho, and R.R. Schrock, *J. Am. Chem. Soc.*, **101**, 5451-5453 (1979).
4. S.J. McLain and R.R. Schrock, *J. Am. Chem. Soc.*, **100**, 1315-1317 (1978).
5. Unpublished results.