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(8) Since the magnitudes of most isotope chemical shifts are a fraction of 1 ppm, it is convenient to express these shifts and their errors in parts per billion (ppb), where 1000 ppb = 1 ppm.
(9) The lack of a temperature dependence eliminates the possibility that the chemical-shift isotope effect arises from changes in the populations of high-energy boat forms of I and I-d_6.
(10) Anet, F. A. L.; Dekmezian, A. H., unpublished works. See also Kivelson, D.; Winstein, S.; Bruck, P.; Hansen, R. L. *J. Am. Chem. Soc.* **1961,** *83,* 2938–2944. These workers showed that abnormal C–H stretching frequencies can arise in compounds where CH groups are sterically compressed.
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(22) Relatively large long-range deuterium chemical-shift isotope effects on the ^{13}C NMR spectrum of cyclodecanone have been reported (Wehrli, F. W.; Jeremić, D.; Mihailović, M. L.; Milosavljević, *J. Chem. Soc., Chem. Commun.* **1978,** *7,* 302–303), but the mechanism and generality of these shifts were not discussed. That these long-range shifts are clearly conformational and not intrinsic follows from the known unsymmetrical conformation of cyclodecanone in solution (Anet, F. A. L.; Cheng, A. K.; Krane, J. *J. Am. Chem. Soc.,* **1973,** *95,* 7877–7878) and is confirmed by a lack of an isotope effect from an α-D on C_6. All of the ^{13}C chemical shifts of the methylene carbons (except C_6) in cyclodecanone are the average of two shifts, as shown by low-temperature NMR measurements. Perturbation of the 1:1 equilibrium by deuterium substitution will therefore affect the chemical shifts at room temperature of all the carbons except C_6, as observed. The deuterium isotope effects found in the low-temperature proton spectra of cyclododecane isotopomers (Anet, F. A. L.; Rawdah, T. *J. Am. Chem. Soc.,* **1978,** *100,* 7810–7814) is also likely to have a conformational origin and to arise from the lack of precise D_4 symmetry in the [3333] conformation of that hydrocarbon.
(23) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1978; pp 107–110.
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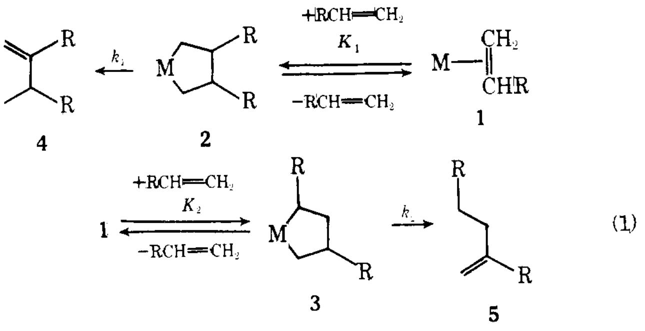
Metallacyclopentane to Metallacyclobutane Ring Contraction

Sir:

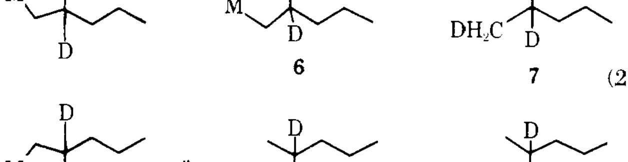
We recently reported that $(\eta^5\text{-}C_5H_5)Cl_2\overline{TaCH_2CHMeCHMeCH_2}$ is the crucial intermediate in the catalytic dimerization of propylene to largely 2,3-dimethyl-1-butene (93%).[1] Unfortunately, this catalyst system becomes inactive after ~20 turnovers, possible because $Ta(\eta^5\text{-}C_5H_5)Cl_2$(propylene), which almost certainly must be formed at some point, is apparently unstable at 25 °C.[2] In contrast, we find that the corresponding $\eta^5\text{-}C_5Me_5$ catalyst system is indefinitely active for dimerizing monosubstituted α olefins[3] (in the absence of air and water), probably because the $Ta(\eta^5\text{-}C_5Me_5)Cl_2(RCH{=}CH_2)$ complexes are comparatively stable and isolable.[2] This communication is concerned with the mechanism of this olefin dimerization reaction.

Table I shows the results of four dimerization reactions.[4,5] Two types of products are formed. The "tail-to-tail" (tt) dimer (**4**, eq 1, M = $(\eta^5\text{-}C_5Me_5)Cl_2Ta$) must come from the trans-β,β'-substituted metallacycle (**2**),[2] while the "head-to-tail" (ht) dimer (**5**) most likely comes from an α,β'-substituted metallacycle (**3**) (stereochemistry unknown). So far, we have observed only **2** spectroscopically (under conditions where dimerization is negligible), even in the last case where only **5** is formed.[8] The drastic change in the ratio of **4** to **5** can be ascribed to marked changes in k_1 and k_2 (and/or K_1 and K_2) under catalytic conditions as R becomes larger (see later).[6]

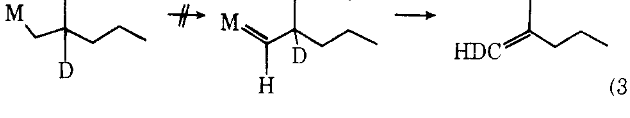


(1)

We chose to study the mechanism of catalytic dimerization using 1-pentene-*2-d* (≥99% d_1). The tt dimer was formed more slowly than that made with unlabeled 1-pentene (k_H/k_D = 3.3

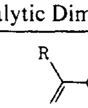
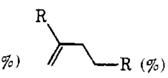


(2)



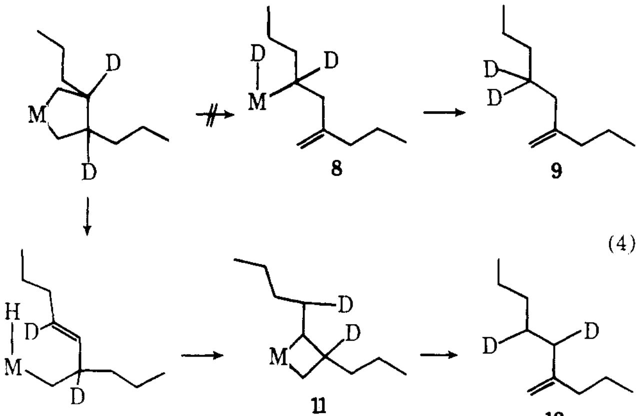
(3)

Table I. Four Catalytic Dimerizations at 50 °C in Toluene[a]

olefin	 (%)	 (%)	k_{obsd} (min^{-1}) × 10^2 [b]
$CH_2{=}CHMe$	98[c]	2[c]	9.4 ± 0.9
$CH_2{=}CHCH_2$-CH_2Me	88[d]	12[d]	8.3 ± 0.8
$CH_2{=}CHCH_2$-$CHMe_2$	61[e]	39[e]	4.9 ± 0.5
$CH_2{=}CHCH_2$-CMe_3	0	100[e]	2.6 ± 0.3

[a] See note 5. [b] See note 6. [c] Identified by GLC coinjection with authentic samples on two different columns. [d] Identified by GLC, ^1H NMR, and ^{13}C NMR comparison with authentic samples. [e] Identified by MS, ^1H NMR, and high-field ^1H gated decoupled ^{13}C NMR.[7]

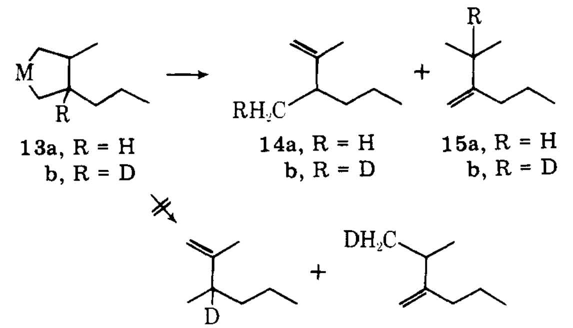
± 0.6) and was shown to be >90% **7** by ^{13}C NMR (eq 2).[9] This result is consistent with formation of a butenyl hydride intermediate (**6**) followed by reductive elimination of the observed product. It is totally inconsistent with an α-hydrogen process such as that shown in eq 3.[10] The labeling in the minor isomer (**12**) is *not* that expected (**9**) by reductive elimination from one of the two possible intermediate butenyl hydrides (**8**, eq 4).



8 **9** **10** **11** **12** (4)

Also, the isotope effect is unexpectedly small (k_H/k_D = 1.2 ± 0.2). The most plausible explanation is that **10** forms and collapses to **11**.[11] **11** is the type of metallacyclobutane complex which we have invoked to explain how (e.g.) propylene reacts with $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$;[12] it is known (in this case) to rearrange exclusively to give the type of product shown. Unfortunately, we cannot tell if **6** also contracts to an MC_3 (metallacyclobutane) complex since the position of the deuterium atoms in the product would be the same. We might suspect that it does since only by invoking an intermediate α,α,β-trimethyltantallacyclobutane complex could we explain the small amount (2% of the mixture) of tetramethylethylene formed when propylene was dimerized using the $\eta^5\text{-}C_5H_5$ catalyst system.[1]

An experiment was designed to test this hypothesis. Codimerization of propylene and 1-pentene yields (in addition to propylene and 1-pentene dimers) four codimers, two of which (**14a** and **15a**, eq 5) come from **13a** and therefore predominate (88% of codimer mix[13a]). Codimerization of propylene and 1-pentene-*2-d* gave **14b** and **15b**, the products expected from the MC_4 to MC_3 ring contraction postulated above, *not* **14c** and **15c**, the products expected from the reductive elimination pathway.[9,13b] (As expected, k_H/k_D for forming **14b** is ~3.5, while that for forming **15b** is ~1.2.) Therefore we conclude that the β,β′-substituted metallacyclopentane complexes, $(\eta^5\text{-}C_5Me_5)Cl_2\overline{TaCH_2CHRCHRCH_2}$, also decompose by forming a metallacyclobutane intermediate which then rearranges selectively to one of two possible olefins.



13a, R = H
b, R = D

14a, R = H
b, R = D

15a, R = H
b, R = D

14c, R = D

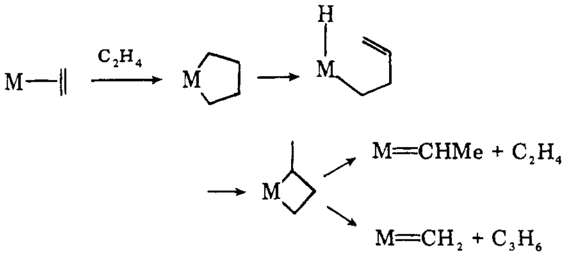
15c, R = D

(5)

We can say from these results that addition of M—H to a butenyl C=C bond is fast relative to reductive elimination. Interestingly, the final step in this sequence of reactions can be viewed simply and consistently as a relatively rapid addition of Ta—H across the C=C bond in a σ-allyl ligand. One therefore need not postulate that "reductive elimination" of the final product from an allyl-hydride complex is rapid and at the same time that reductive elimination from a butenyl-hydride complex is relatively slow.

What we cannot yet say is that formation of the butenyl-hydride complex is the slowest step. In fact, that may more often be a preequilibrium step. The overall rate therefore also would depend on the rate of ring contraction. This would nicely explain why some bicyclic species[1] are so stable; the strained metallacyclobutane complex would form less readily. Interestingly, one might then suspect that the required metallacyclobutane intermediate from **2** would become more difficult to make and that from **3** easier to make as R gets larger; i.e., k_1 decreases and k_2 increases. This would help explain the switchover from tt dimer to ht dimer (Table I).

These results have two implications. First, it is quite likely that all tantalum metallacyclopentane complexes, and at least other early transition metal d^0 MC_4 species that decompose to give products of an apparent β-elimination sequence, decompose via metallacyclobutane intermediates. Secondly (but more speculatively), the $MC_4 \rightarrow MC_3$ ring contraction is a straightforward and reasonable way of forming an alkylidene ligand from olefins (eq 6, using ethylene as the example) assuming that some MC_3 complexes which form in this manner will cleave to give metathesis-type products instead of rearranging. One thereby can not only explain how some alkylidene ligands are formed in olefin metathesis systems[14] which involve alkylating agents (since that is precisely how we form complexes of the type $Ta(\eta^5\text{-}C_5Me_5)Cl_2(CH_2{=}CHMe)^2$), but also how they form when no alkylating agent is present (e.g., M = Mo(2+), Mo(0), W(4+), etc.).



(6)

Acknowledgments. We thank the National Science Foundation (CHE76-07410) for support, the Francis Bitter National Magnet Laboratory for use of their high-field NMR facilities, and G. M. Whitesides for use of his GLC/MS facilities.

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(1) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978,** *100,* 1315.
(2) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979,** *101,* 4558.

(3) The largest scale dimerization reaction which we have done gave 1258 mol of dimer/mol of catalyst. Purple $Ta(\eta^5\text{-}C_5Me_5)Cl_2(1\text{-octene})$ (115 mg, 0.26 mmol) was added to 77.7 g (0.692 mol) of dry, O_2-free 1-octene to give a light orange color characteristic of a metallacyclopentane complex. After the mixture was heated at 100 °C for 20 h, the color was dark orange. GLC analysis showed that >97% of the product consisted of two dimers (see text). (A separate experiment showed that these initial products isomerize slowly after all of the monomer is consumed.) The mixture was passed through a short column of alumina to remove tantalum and vacuum distilled to give a 97% isolated yield of the dimer mixture.

(4) A typical dimerization reaction is done in 3 mL of toluene employing 0.2 mmol of any $Ta(\eta^5\text{-}C_5Me_5)Cl_2(\text{olefin})$ complex (usually the olefin is cyclooctene;[2] it is displaced by the α olefin and is otherwise inert) and 8.0 mmol of the primary olefin in a small glass pressure vessel joined to a metal pressure head by an O-ring seal. Samples are removed through a small septum. The temperature was controlled to ±0.5 °C with an oil bath. Rates are reproducible usually within the ±10% estimated error range (Table I). We have shown that this reaction is first order in $[Ta]_T$ and, under conditions where K_1 and/or K_2 (eq 1) are large (e.g., for propylene), independent of olefin concentration. The rate of propylene dimerization is also independent of solvent (toluene, decane, ether, chlorobenzene).

(5) The dimerization reactions shown in Table I employed $Ta(\eta^5\text{-}C_5Me_5)(\text{cyclooctene})Cl_2$ (0.07 M) as the catalyst; [olefin] = 2.8 M except propylene = 40 psi.

(6) The $k_{obsd} = \{(k_1K_1 + k_2K_2)[ol]\}/\{1 + K_1[ol] + K_2[ol]\}$ assuming that **2** → **4** and **3** → **5** are the slowest steps. By varying the olefin concentration and/or by making several assumptions, we will be able to estimate values for k_1, K_1, k_2, and K_2 in several cases. These data are still being gathered and will be discussed fully later.

(7) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden and Sons, Ltd.: London, 1978.

(8) After a mixture of 1.40 mmol of $Ta(\eta^5\text{-}C_5Me_5)Cl_2(Me_3CCH_2CH{=}CH_2)$ and 5.60 mmol of $Me_3CCH_2CH{=}CH_2$ in 1.5 mL of toluene-d_8 was stored at 0 °C (where the dimerization rate is negligible) for 24 h, a ^{13}C NMR spectrum showed it to consist of about three parts metallacycle **2** ($R = CH_2CMe_3$) and one part **1**. If we assume that equilibration is complete, then $K_1 \approx 1.5$ at 0 °C. The equilibrium between **2** and **1** lies well toward **2** in the other three cases at 10 °C. We are in the process of looking for **3** in a favorable case under catalytic conditions.

(9) All carbon atoms except those in the two methyl groups furthest from the double bond can be identified (at 67.89 MHz) by peak multiplicity plus empirical chemical shift additivity rules[7] which are known to be (and can be shown to be for several authentic samples here) accurate and reliable for simple hydrocarbons. We estimate that we could see 5–10% of a carbon atom to which no D was attached since it has a significantly different chemical shift at this field strength.

(10) Schrock, R. R. *Acc. Chem. Res.* **1979,** *12,* 98.

(11) An alternative explanation which both referees offered is formation of a diene–TaHD complex by a (simultaneous?) double β-hydrogen elimination followed by addition to one double bond to give **12**, all stereospecifically. Phenomenologically the result is the same. We still think our proposed mechanism is more plausible.

(12) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1977,** *99,* 3519.

(13) (a) These two olefins were prepared from the commercially available ketones. They were identical with the two major codimers by GLC and ^{13}C NMR. (b) These two products were inseparable by preparative GLC. Therefore, the labeling had to be determined using the isolated mixture. The major component (**15b**), could be identified by the 1:1:1 triplet for the aliphatic tertiary carbon atom. Since the 1:1:1 triplet for the labeled methyl carbon atom in **14b** overlaps partially with another peak, we could not be so certain of the amount of D on this carbon atom; however, the signal for the aliphatic tertiary carbon atom is a strong singlet as it should be.

(14) (a) Haines, R. J.; Leigh, G. J. *Chem. Soc. Rev.* **1975,** *4,* 155. (b) Calderon, N.; Ofstead, E. A.; Judy, W. A. *Angew. Chem., Int. Ed. Engl.* **1976,** *15,* 401. (c) Grubbs, R. H. *Prog. Inorg. Chem.* **1978,** *24,* 1. (d) Katz, T. J. *Adv. Organomet. Chem.* **1977,** *16,* 283. (e) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Ibid.,* **1979,** *17,* 449.

(15) (a) NSF Predoctoral Fellow, 1975–1978. (b) ITP Postdoctoral Fellow (Spain), 1976–. (c) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1978.

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Satellite Structure in the X-ray Photoelectron Spectra of Metal Complexes of Alkyl Isocyanides[1]

Sir:

Shake-up satellite structure[2,3] associated with the X-ray photoelectron spectra (XPES) of transition metal complexes is important because it is frequently related to the energy differences between filled and unfilled molecular orbitals. While such satellites are quite common for salts and complexes of many first-row transition metal ions,[2,3] they have been rarely encountered with the second- and third-row transition metal ions.[2,3] The major exception to this latter experimental observation is the shake-up satellites which are observed in the XPES of certain carbonyls of the second and third transition series.[4-6] For example, satellites seen between 5 and 6 eV on the O 1s, C 1s, and metal (Cr 2p, Mo 3d, or W 4f) levels of $M(CO)_6$, where M = Cr, Mo or W, are believed to be a consequence of a metal(d) → $CO(\pi^*)$ charge-transfer transition.[5] These observations, and their attendant interpretation, naturally lead to the question of whether those molecules which are formally isoelectronic with these carbonyls might exhibit related satellite structure.

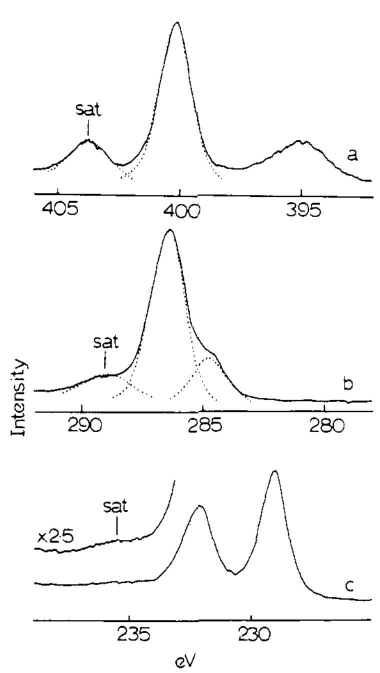

Figure 1. X-ray photoelectron spectra of $[Mo(CNCH_3)_7](PF_6)_2$: (a) N 1s (the Mo $3p_{3/2}$ peak is at 395 eV); (b) C 1s; (c) Mo 3d. Deconvolutions were carried out using the procedure described in ref 11.

In view of the isoelectronic relationship between CO and CNR, the possibility that shake-up satellites might be found in the XPES of transition metal isocyanides makes the latter species of considerable spectroscopic interest. However, while the XPES of certain isocyanide complexes have been reported, for example, $Ni(CNBu^t)_4$, $[M(CNCH_3)_4](PF_6)_2$, and $[M_2(CNCH_3)_6](PF_6)_2$, where M = Pd or Pt,[7-9] such satellites have not previously been detected. We now report the existence of satellites in the XPES of the seven-coordinate molybdenum(II) complexes $[Mo(CNR)_7](PF_6)_2$, where $R = CH_3$, $C(CH_3)_3$, or C_6H_{11},[10] species which are formally isoelectronic with $Mo(CO)_6$.[13]

The N 1s spectra of all three complexes are virtually identical with the primary photoline at 399.9 ± 0.1 eV (fwhm of 1.5–1.7 eV) and a satellite at 403.6 ± 0.2 eV (Figure 1). The observation of a satellite in the N 1s XPES of all three complexes,[14] the constancy of the intensity ratio I_s/I_p for the satellite and primary photoline (0.18 ± 0.04) and the invariance of the spectra with differences in the X-ray flux and irradiation times makes us confident that we are observing genuine satellite structure rather than the formation of a high oxidation state nitrogen-containing contaminant (such as nitrite).

If the above interpretation is correct, one might expect to find, based on the data for transition metal carbonyls,[5,6] a satellite in the C 1s region of similar magnitude and energy separation from the primary photoline. As shown in Figure 1, this is in fact the case. For $[Mo(CNCH_3)_7](PF_6)_2$, the C 1s

0002-7863/79/1501-5453$01.00/0