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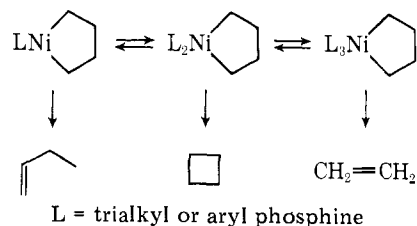
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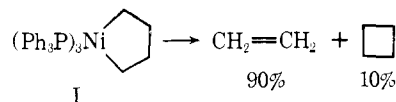
The Relationship between Metallacyclopentanes and Bis(olefin)-Metal Complexes

Sir:

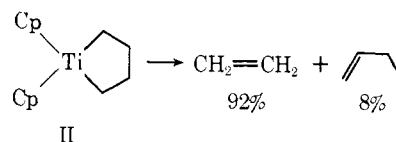
Metallacyclopentanes appear to be intermediates in a number of olefin dimerization reactions.^{1,2} We recently reported that phosphine-nickelacyclopentanes decompose by reductive elimination, β -hydride elimination, or C-C bond cleavage depending on the coordination number of the complex.³



The most surprising observation was the production of ethylene from the highest coordination number complexes.



Tetramethylenetitanocene (II) also has been observed to decompose to produce ethylene in good yield.⁴



We now have evidence that both of these complexes decompose by reversible carbon-carbon bond cleavage to produce an intermediate bis(ethylene) complex. This process can be detected by labeling two of the equivalent carbons of the metallacycle since the two carbons of the olefin should become equivalent in the intermediate.

Consequently, 2,2,5,5-tetradeuteriometallacycles of nickel and titanocene were prepared. Equilibration of the metallacycle with the bis(olefin) complex should result in the production of the 2,2,4,4- and 3,3,4,4-*d*₄ isomers (Scheme I). Hydride rearrangements would result in the production of isomers containing only one deuterium per carbon.⁵

Since the bromination and protonolysis of metallacycle produces quantitative yields of 1,4-dibromobutane or butane,^{3,4} the labeling of the metallacycle can be analyzed by determining

Table I. Isomerization of Phosphine-Nickelacyclopentane in Toluene

Compd	Temp, °C	Time, h	Butane- <i>d</i> ₄ , mol % ^a				% isom ^c	% dec
			1,1,4,4	1,1,3,3	2,2,3,3	Others ^b		
1. III- <i>d</i> ₄ ^e	10	1	98.3	0	0	1.7	0	
2. I- <i>d</i> ₄ ^f	-30	0	95.2	2.4	1.2	1.2	4.8 (3.6 ^d)	0
3. I- <i>d</i> ₄ ^f	0	0.5	84.3	7.0	2.6	6.0	13.2 (13.3) ^d	7.4
4. I- <i>d</i> ₄ ^f	0	1.0	47.0	29.7	16.1	7.2	66.7 (65.1) ^d	17.0
5. I- <i>d</i> ₄ ^f + 4.5PPh ₃	0	1.0	70.9	15.3	8.1	5.7	33.4	14.8
6. I- <i>d</i> ₄ ^f + 6.9PPh ₃	0	1.0	84.7	7.4	3.6	4.3	15.2	13.6
7. I- <i>d</i> ₄ ^f + 8.0PPh ₃	0	1.0	89.2	5.9	2.9	2.1	12.0 (13.7) ^d	13.0
8. I- <i>d</i> ₄ ^g	25	2.0	9.6	16.7	8.7	65.0	97.4	

^a Relative product yield of chromatographically pure butane-*d*₄ isomer. ^b These isomers include deuterium-scrambled butane-*d*₄ isomers such as butane-1,1,3,4-, -1,2,3,3-, and -1,2,3,4-*d*₄. ^c Relative percentage of the nickelacyclopentane isomerization was obtained as follows:

$$\frac{[1,1,3,3] + 2[2,2,3,3]}{[1,1,4,4] + [1,1,3,3] + [2,2,3,3]} \times 100$$

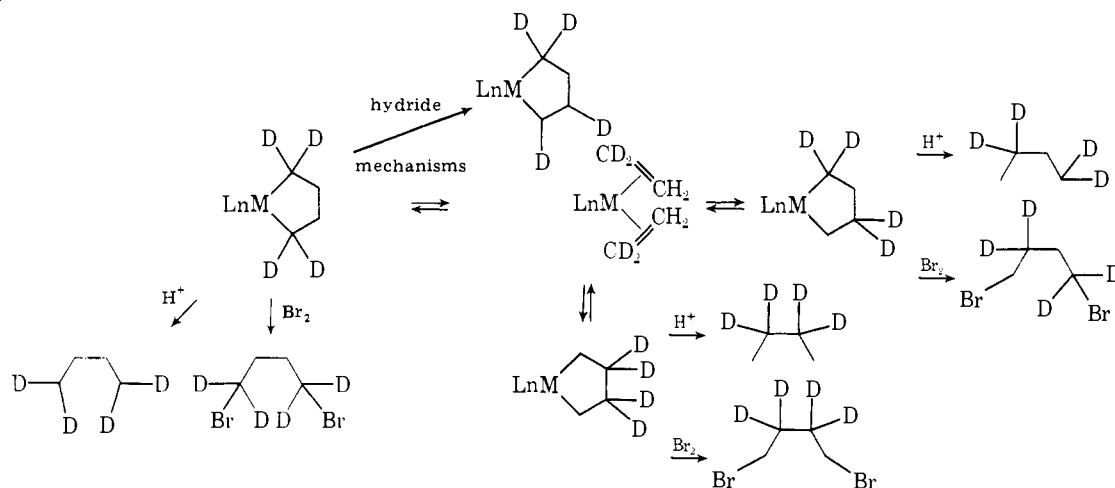
^d These values were obtained by ¹H NMR analysis of 1,4-dibromobutane-*d*₄ afforded on the reaction of the complex with Br₂. ^e 0.044 M toluene solution. ^f 0.00231 M toluene solution. ^g 0.054 M toluene solution.

Table II. Isomerization of Titanacenacyclopentane in Toluene

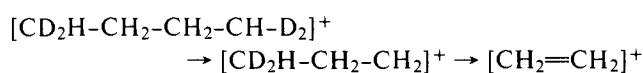
Compd	Temp, °C	Time, h	Butane- <i>d</i> ₄ , mol % ^a				% isom ^c	% dec
			1,1,4,4	1,1,3,3	2,2,3,3	Others ^b		
9. II- <i>d</i> ₄ ^e	-60	0	84.7	6.8	2.5	6.0	12.6	0
10. II- <i>d</i> ₄ ^e	-35	0.5	79.6	9.7	5.1	5.6	21.1	3
11. II- <i>d</i> ₄ ^e	-35	1.0	73.0	10.7	5.9	10.4	25.1	~3
12. II- <i>d</i> ₄ ^e	-45	3.0	68.0	14.4	7.5	10.0	32.73 (31.2) ^d	~5

^{a-d} See comparable footnotes in Table I. ^e 0.08 M toluene solution.

Scheme I

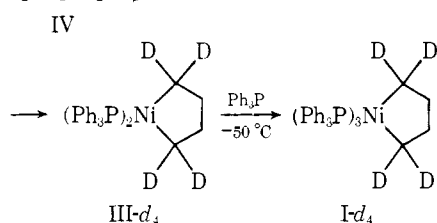
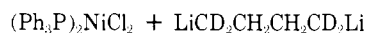


the labeling pattern of the butanes produced by this reaction. The labeling pattern of *n*-butane-*d*₄ can be determined from the analysis of the cracking pattern in the mass spectrometer. Butanes fragment by the following process:⁶



The labeling pattern of the mixtures was calculated on the basis of this scheme.⁷ As confirmation of the mass spectral assignments, the positions of the labels in the 1,4-dibromobutanes were determined by NMR. Since the protons at carbon 1 and 4 are distinct in the ¹H NMR from those at carbons 2 and 3, the percent isomerization can be determined from the relative integral of the two signals.⁸ This technique does not distinguish between the pairwise and monohydride isomerization of the labels.

Bis(triphenylphosphine)tetramethylenenickel(II)-2,2-,5,5-*d*₄ (I-*d*₄) was prepared from the corresponding nickel dihalide and 1,4-dilithiobutane-1,1,4,4-*d*₄ (98.0% isotopic purity)⁹ and converted into the crystalline trisphosphine complex at -50 °C.³ The same dilithium reagent was used to prepare the labeled titanacyclopentane.⁴



Solutions of the complexes in toluene were maintained at low temperature for time periods which resulted in a low percentage of decomposition. The solutions were then mixed with dry hydrogen chloride or bromine at -30 ~ -40 °C and the C₄ products were purified by gas chromatography and then analyzed. The amounts of isomerization, decomposition, and scrambling (monohydride rearrangements) are listed in Tables I and II.

Confirmation of the intramolecular nature of the reaction was obtained by mixing equal amounts of I and I-*d*₄ in toluene at 0 °C for 2 h (sufficient time for extensive isomerization) before protonolysis. Only butane-*d*₄ and *d*₀ are produced.¹⁰ Intermolecular exchange and isomerization would have produced butane-*d*₂. These results demonstrate a number of general features of metallacyclopentanes of both early and late transition elements.

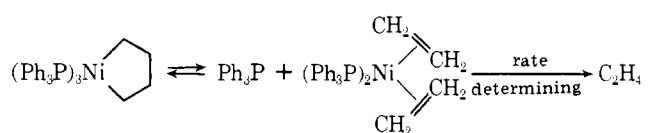
The rate of isomerization of both complexes was faster than

the decomposition to produce ethylene. This is most consistent with an equilibrium between the metallacycle and bis(olefin) complex with the decomposition of the bis(olefin) complex being rate determining.

Since the ratio of the 2,2,4,4 to 3,3,4,4 isomer was near 2:1 (the equilibrium ratio) even at low conversions, the intermediate must be symmetrical, or more likely the rotation of the olefins⁹ in the intermediate was faster than recyclization.

The bis(triphenylphosphine)nickel complex (III-*d*₄) which does not decompose to yield ethylene as a major product did not produce isomerized metallacycles. This complex under conditions similar to the analogous trisphosphine complex (I-*d*₄) only produced a low percentage of monohydride scrambled products. For those complexes which produced ethylene as the major decomposition product, isomerization (D₂ units move pairwise) was faster than scrambling.

If the trisphosphine nickelacycle decomposed to a bis(olefin) complex, a 20-electron system would have been produced (five-coordinate nickel(0)). Consequently, it is reasonable to assume that a phosphine is lost prior to or concurrent with the carbon-carbon bond cleavage. The observation (Table I) that the rate of isomerization decreased on addition of excess triphenylphosphine shows this to be the case. The lower coordination number intermediate cannot be the square-planar structure III, since it does not isomerize. The equilibrium in the equation may involve one or more intermediates.



The above results and those beginning to appear in the literature suggest that the equilibrium between bis(olefin) complexes and metallacyclopentanes¹¹ is a much more general reaction than thought in the past and may be a key reaction in a number of metal-catalyzed reactions of olefins.

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$$[2,2,3,3] = (m/e\ 32)/0.239$$

$$[\text{scrambled isomers}] = x = (m/e\ 46) - [2,2,3,3]0.129 - [1,1,4,4]0.057 - [1,1,3,3]0.18$$

$$[1,1,3,3] = 2[(m/e\ 47) - [2,2,3,3] - X]0.18 - 0.028[1,1,4,4]$$

$$[1,1,4,4] = (m/e\ 45) - [1,1,3,3]0.568 - [2,2,3,3]0.136 - 0.247X$$

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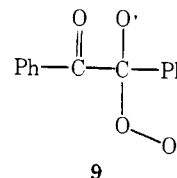
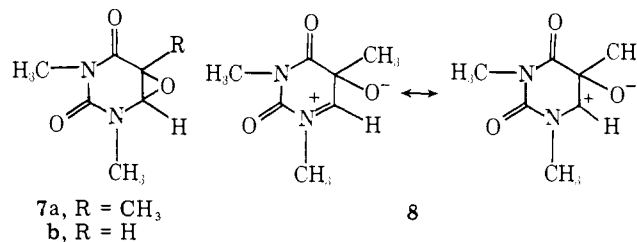
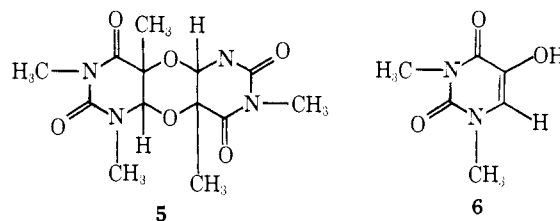
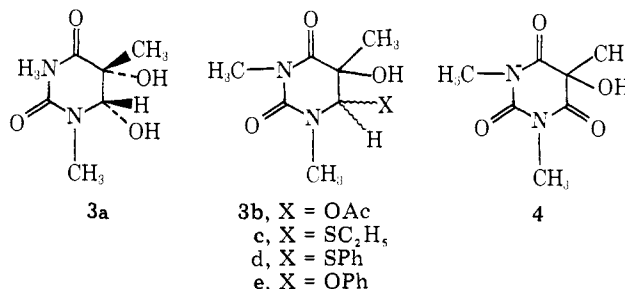
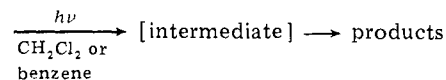
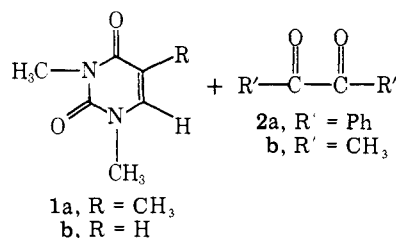
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α -Diketone Sensitized Photooxidation of Pyrimidines

Sir:

Because of possible biological implications, the photosensitized oxidation of nucleic acids and their components has been extensively studied.¹ It was noted^{1b} that in most cases the primary products of nucleic acid components are not well known because of the complexity of product mixtures and the tendency of initial products to undergo further reactions. In general, dye-sensitized photooxidation of simple olefins yields allyl hydroperoxides and/or dioxetanes which are believed to result from the interaction of the substrate molecules with singlet oxygen.^{1b} However, Shimizu and Bartlett² have found that epoxides were produced as main products when α -diketones were used as sensitizers. They have shown that this photooxidation is quite different from that mediated by singlet oxygen and, also, from radical-chain autooxidations. This interesting finding prompted us to undertake a study of α -diketone sensitized oxidation of pyrimidines³ because epoxidation of the nucleic acid components might be one of the initial oxidation reactions responsible for oxidative damage occurring in *in vivo* systems and because current findings in the study of organic epoxides⁴ indicate their considerable importance in relation to biochemistry and environmental chemistry.^{1b}

A CH_2Cl_2 solution of equimolar amounts (0.05 M) of 1,3-dimethylthymine (**1a**, Me_2Thy) and benzil (**2a**) was irradiated⁵ for 1 h. The solvent was removed, and the products, separated by TLC on silica gel with eluent $CHCl_3:CH_3CN$ (7:3), were found to be *cis*- Me_2Thy glycol (**3a**, 60%),⁶ 5-methyl-5-hydroxybarbituric acid (**4**, 10%),⁷ and (2,3),(6,5)-*diMe_2Thy*-1,4-dioxane (**5**, 3%).⁸ No *trans* glycol could be detected. Using biacetyl (**2b**, 0.5 M) in place of **2a** and benzene as the solvent,⁹ the reaction gave **3b** (**3a** 6-acetate, 85%)⁹ in a regio- and stereospecific manner, and neither **3a** nor **5** was found. Postirradiation treatment of the former reaction mixture with acetic acid also gave **3b** (80%), but such a treatment of **3a** or **5** resulted in no reaction. Similar postirradiation treatment with thioethanol and thiophenol gave **3c** (90%)¹⁰



and **3d** (90%),¹¹ respectively, whereas treatment with phenol yielded two isomers of **3e** (80%)¹² in approximately a 3:2 ratio.

These findings could be readily explained by assuming that pyrimidine epoxide (**7**) is the initial product. Its instability or reactivity may stem from the presence of a nitrogen atom α to the epoxide ring. The isolation of dihydropyrimidine derivatives (**3**) may result from the ring opening of an epoxide by various nucleophiles. The formation of **5** is particularly interesting because **5** is a dimeric product of **7** and is analogous to the commonly known formation of 1,4-dioxane from ethylene oxide.

Photosensitized oxidation of dimethyluracil (**1b**) with **2a** or **2b** was also studied and only 1,3-dimethylisobarbituric acid (**6**, 40%)¹³ was obtained. Assuming that a corresponding epoxidation occurred, **6** is probably produced either directly from **7** by a hydride transfer¹⁴ or through *cis*-uracil glycol which is known to convert readily to isobarbituric acid.¹⁵

Even though the stereochemistry of **3b-e** has not been determined, the stereospecific formation of a *cis* diol (**3a**) is in-