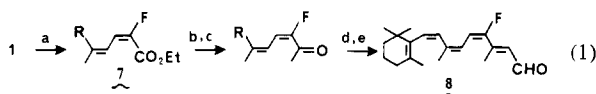


Scheme II



<sup>a</sup> (EtO)<sub>2</sub>POCFHCO<sub>2</sub>Et, 9, LDA. <sup>b</sup> MeOH/KOH. <sup>c</sup> MeLi.  
<sup>d</sup> (EtO)<sub>2</sub>POCH<sub>2</sub>CO<sub>2</sub>Me, NaH, C<sub>6</sub>H<sub>5</sub>/DMF (9:1). <sup>e</sup> LiAlH<sub>4</sub>  
 (-78 °C); MnO<sub>2</sub> (R = *cis*-C<sub>11</sub>H<sub>17</sub>).

*all-cis*-retinal via consecutive six-electron electrocyclic reactions known for all retinal isomers containing the 11-*cis*,13-*cis* geometry.<sup>3,5,7</sup> The <sup>1</sup>H NMR spectrum of the major product was that of a new retinal isomer. At 300 MHz, its spectrum was of first order, thus peaks readily were assignable. The assignments were confirmed by selective decoupling experiments. The chemical shifts of CH<sub>3</sub>-5, H<sub>8</sub>, and CH<sub>3</sub>-13 revealed respectively the 7-*cis*, 9-*cis*, and 13-*trans* geometry while the magnitudes of *J*<sub>7,8</sub> and *J*<sub>11,12</sub> were consistent only with the *cis* geometry at both centers. Therefore, the new isomer must be 7-*cis*,9-*cis*,11-*cis*-retinal (4C). The UV spectrum (Figure 1) displayed features similar to those of 7-*cis*,11-*cis*-retinal.<sup>5</sup>

*all-cis*-Retinol (5B) was obtained in quantitative yield by reduction of ethyl *all-cis*-retinoate (5A) by Dibal-H at -70 °C. Its <sup>1</sup>H NMR spectrum was readily assigned after selective decoupling experiments. The magnitude of the vinyl coupling constants and chemical shifts of the vinyl and CH<sub>2</sub>-15 hydrogens showed retention of the *all-cis* geometry.<sup>10b</sup> The compound, a colorless oil, was found to be stable even after several months of storage at 0 °C under nitrogen.

As in the case of other hindered isomers of retinal,<sup>5,6,11</sup> 7-*cis*,9-*cis*,11-*cis*-retinal was found to give a low yield (28%) of a pigment analogue (see Figure 1 for the difference absorption spectrum) when incubated with a digitonin solution of bovine opsin. The slow rate of pigment formation, *k*<sub>2</sub> = 0.02 M<sup>-1</sup> s<sup>-1</sup>, is similar to that of 7-*cis*,11-*cis*-retinal.<sup>12</sup> Properties of the pigment analogue including the photobleaching characteristics will be examined in detail.

We have also prepared a fluorinated analogue of the tri-*cis* isomer 7-*cis*,9-*cis*,11-*cis*-12-fluororetinal, 8 (7Z,9Z,11E,13E), Scheme II. As observed earlier,<sup>13</sup> reaction of the fluoro-C<sub>2</sub>-phosphonate, 9, gave preferentially the *cis* geometry (12E) at the newly formed double bond. The isolated C<sub>17</sub>-fluoro ester, 7, (flash column chromatography) was elaborated in the conventional fashion (17 + 1 + 2).<sup>13</sup> The conditions for the C<sub>2</sub>-chain-extension reaction was for selective formation of the 13-*trans* geometry.<sup>5</sup> Assignment of the tri-*cis* geometry was again by its NMR data and by comparison with those of the other known isomers.<sup>13</sup>

In summary, the current effort not only brings to a conclusion of preparation of stereoisomers of vitamin A but also demonstrates further the stability of the hindered isomers, which was once questioned.<sup>14</sup>

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**Supplementary Material Available:** <sup>1</sup>H NMR data of *all-cis*-C<sub>18</sub>-ketone, 7-*cis*,9-*cis*,11-*cis*- and *all-cis*-vitamin A, and 12-fluoro-7-*cis*,9-*cis*,11-*cis*-retinal, the complete <sup>1</sup>H NMR spectrum of 7-*cis*,9-*cis*,11-*cis*-retinal and selective decoupled vinyl signals, and chromatographic separation conditions (3 pages). Ordering information is given on any current masthead page.

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## Stereochemistry of the Olefin Metathesis Reaction: Theoretical Extended Hückel Study of Substituted Metallacyclobutanes

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It has been claimed that the stereochemistry of the olefin metathesis reaction is governed by the various interactions occurring in the puckered metallacyclobutane intermediate.<sup>1-6</sup> This assumption was largely based on experimental data related to the metathesis of various olefins with group 6 metal-based catalysts.<sup>5,6</sup> The hypothesis of ring puckering was deduced from structural data related to a series of stable substituted or unsubstituted platinacyclobutanes.<sup>7,8</sup> Recent X-ray studies of a titanacyclobutane complex Cp<sub>2</sub>TiCH<sub>2</sub>CHRCH<sub>2</sub> (R = phenyl) indicate that

a metallacyclobutane complex may be planar and may exhibit a moderate degree of activity and stereoselectivity in metathesis.<sup>9,10</sup> A similar system, Cl<sub>2</sub>TiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, studied by Goddard<sup>11</sup> using *ab initio* calculations was found to be planar. However, both systems have no substituents in the 1-3-positions. One may reasonably assume that if substituents were present in the 1-3-positions, a certain degree of puckering could have occurred.<sup>12</sup> It was therefore necessary to investigate (i) whether or not the presence of substituents in the metallacycle will favor a puckered conformation, (ii) what the favored conformations with substituents in the 1-2- or 1-3-positions are, and (iii) what the effect of the group 6 transition metal is.

As model of our extended Hückel calculations we took a six-coordinate metallacyclobutane complex, Cl<sub>4</sub>MCHR<sub>1</sub>CHR<sub>2</sub>CHR<sub>3</sub> (M = Cr, W; R<sub>1</sub> = CH<sub>3</sub>; R<sub>2</sub> = H, CH<sub>3</sub>; R<sub>3</sub> = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) for which the d<sup>4</sup> electron count is assumed to be the most favored configuration.<sup>13</sup> The metallacyclobutane was assumed to be pseudooctahedral with classical M-C, M-Cl, and C-C bond lengths values,<sup>14</sup> with a C<sub>1</sub>-M-C<sub>3</sub> angle close to that found in

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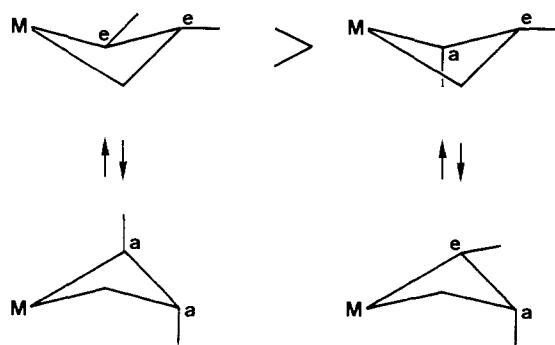
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Scheme I



Scheme II

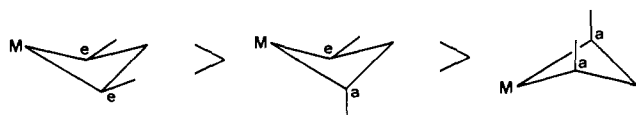


Table I. Effect of Methyl Substituents in the 1-2-Positions on Total Energy (eV) of Metallacyclobutane

conformation	puckering angle, deg				
	M = W			M = Cr	
	0	12	40	0	12
1e-2a <sup>a</sup>	-1155.19	-1153.26	-1148.84	-1154.22	-1153.28
1a-2e <sup>a</sup>	-1155.19	-1155.99	-1157.05	-1154.22	-1154.45
1a-2a <sup>b</sup>	-1157.72	-1155.45	-1151.10	-1156.52	-1154.19
1e-2e <sup>b</sup>	-1157.72	-1158.60	-1158.74	-1156.52	-1157.63

<sup>a</sup> Cis-directing conformation. <sup>b</sup> Trans-directing conformation.

### CP<sub>2</sub>TiCH<sub>2</sub>CRR'CH<sub>2</sub><sup>10</sup> or L<sub>2</sub>Cl<sub>2</sub>PtCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sup>7</sup>

It has been postulated that the trans stereoselectivity observed in metathesis of  $\alpha$ -olefins was due to the favored 1-2 e-e conformation with respect to the 1-2 a-e conformation of the substituted metallacycle<sup>5,6</sup> (Scheme I).

Calculations (Table I) are in agreement with such prediction since the most stable conformation is the e-e one. Besides, the planar conformation appears not to be the most stable one.

The retention of configuration of the starting olefin in metathesis of acyclic olefins is usually ascribed to the occurrence of a 1-3 diaxial interaction<sup>1-6</sup> (Scheme II).

By comparing the stabilities of the planar and puckered conformations, it appears that the most stable one is the puckered 1e-3e conformation (Tables II and III).

In group 6, chromium-based catalysts are more stereoselective than molybdenum-based catalysts, which are more stereoselective than tungsten-based catalysts.<sup>5</sup> This effect has been tentatively explained on the basis of the decrease of the M-C distance of the metallacycle in the order W > Mo > Cr. A simultaneous increase in the 1-3 interaction would result from such shortening of the M-C  $\sigma$ -bond. This trend is also apparent from the calculations: the energy difference between the 1e-3e and the 1e-3a conformation is more pronounced with chromium than with tungsten. It appears also that regardless of their conformations, chromia-cyclobutanes are less stable than tungstacyclobutanes, which is in rough agreement with ab initio calculations of Goddard carried out with similar systems.<sup>17,18</sup>

In conclusion, from these extended Hückel calculations it appears that (i) the presence of substituents in a metallacycle of the type Cl<sub>4</sub>MCHR<sub>1</sub>CHR<sub>2</sub>CHR<sub>3</sub> will favor a puckered conformation, (ii) with a 1-2-substituted metallacycle, the favored conformation is the 1e-2e one, (iii) with a 1-3-substituted metallacycle, the

Table II. Effect of Methyl Substituents in the 1-3-positions on Total Energy (eV) of Metallacyclobutane

conformation	puckering angle, deg				
	M = W			M = Cr	
	0	12	40	0	12
1e-3a <sup>a</sup>	-1157.02	-1157.03	-1156.86	-1153.91	-1153.99
1a-3a <sup>b</sup>	-1156.97	-1156.63	-1155.49	-1153.81	-1152.89
1e-3e <sup>b</sup>	-1156.97	-1157.31	-1157.71	-1153.81	-1154.89

<sup>a</sup> This conformation does not result in a retention of the configuration of the starting *cis*- or *trans*-olefin. <sup>b</sup> These conformations result in a retention of the configuration of the starting *cis*- or *trans*-olefin.

Table III. Effect of Methyl Substituent in the 1-Position and Ethyl Substituent in the 3-Position on Total Energy (eV) of Metallacyclobutane (M = W)

conformation	puckering angle, deg		
	0	10	20
1Mee-3Eta <sup>a</sup>	-1263.67	-1263.71	-1263.79
1Mea-3Ete <sup>a</sup>	-1263.67	-1263.70	-1263.79
1Mea-3Eta <sup>b</sup>	-1263.62	-1263.35	-1263.11
1Mee-3Ete <sup>b</sup>	-1263.62	-1263.95	-1264.30

<sup>a</sup> These conformations do not result in a retention of the configuration of the starting *cis*- or *trans*-olefin. <sup>b</sup> These conformations result in a retention of the configuration of the starting *cis*- or *trans*-olefin.

favored conformation is the 1e-3e one, (iv) the 1-2 interactions, which favor the formation of trans products regardless of the *cis* or *trans* nature of the starting olefin, are more pronounced than the 1-3 interactions, in good agreement with Calderon's experiments with very bulky olefins,<sup>6</sup> and (v) the effects are more pronounced with chromium than with tungsten.

These results are in good qualitative agreement with the results of the literature concerning the stereochemistry of metathesis of internal or terminal olefins. Further studies are in progress to investigate simultaneously those effects in the case of *cis*- and *trans*-2-pentene<sup>5</sup> as well as *cis*- or *trans*-4-methyl-2-pentene metathesis.<sup>6</sup>

## Surface Acid Site Characterization by means of CP/MAS Nitrogen-15 NMR

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The surface properties of heterogeneous solids with catalytic activity are of continuing interest with respect both to the nature of the active sites and to how these sites are modified by chemical or physical treatment. The presence of both Brønsted and Lewis acid sites in solid catalysts has been inferred from infrared spectroscopic studies,<sup>1-3</sup> and attempts have been made to study such active sites by means of <sup>1</sup>H<sup>3</sup> and <sup>13</sup>C NMR.<sup>4,5</sup> On considering the large nuclear shielding range that <sup>15</sup>N NMR presents,<sup>6</sup> use of this nucleus becomes an attractive possibility in studies of this

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