

- (12) Rondan, N. G.; Houk, K. N., private communication.  
 (13) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333.  
 (14) Moss, R. A.; Mallon, C. B.; Ho, C.-T. *J. Am. Chem. Soc.* **1977**, *99*, 4105.  
 (15) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.  
 (16) Equation 2 is normalized to  $m_{\text{CCl}_2} = 1.00$ , giving it an electrophilic heritage. Indeed,  $m_{\text{CXY}}^{\text{calcd}}$  for 12 carbenes, including  $(\text{CH}_3\text{O})_2\text{C}$ , correlates linearly with 4-3 IG calculated values of  $E_{\text{CXY}}^{\text{LUMO}}$ .<sup>7</sup>  $(\text{CH}_3\text{O})_2\text{C}$  does not add to simple alkenes,<sup>3</sup> so that  $m_{(\text{CH}_3\text{O})_2\text{C}}$  is an "imaginary" selectivity index. Nevertheless, it serves to locate the *m* region in which nucleophilic carbenes reside.  
 (17) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.  
 (18) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.  
 (19) Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937.  
 (20) An analogous situation holds for  $\text{CH}_3\text{OCCl}$  and *t*-MeCH=CHMe.  
 (21) An analogous situation holds for  $\text{CH}_3\text{OCCl}$  and  $\text{CH}_2=\text{CHCOOMe}$ .  
 (22) With  $(\text{CH}_3\text{O})_2\text{C}$  ( $E^{\text{LU}} = 4.09$ ,  $E^{\text{HO}} = -10.81$  eV),<sup>7</sup> ( $E_{\text{alk}}^{\text{LU}} - E_{\text{CXY}}^{\text{HO}}$ ) is less than ( $E_{\text{CXY}}^{\text{LU}} - E_{\text{alk}}^{\text{HO}}$ ) for  $\text{CH}_2=\text{CHCN}$ ,  $\text{CH}_2=\text{CHCOOMe}$ , *t*-MeCH=CHMe, and  $\text{Me}_2\text{C}=\text{CH}_2$  (i.e., these could be termed "nucleophilic" additions). However, with  $\text{Me}_2\text{C}=\text{CMe}_2$ , ( $E_{\text{CXY}}^{\text{LU}} - E_{\text{alk}}^{\text{HO}} = 12.36$  eV) is less than ( $E_{\text{alk}}^{\text{LU}} - E_{\text{CXY}}^{\text{HO}} = 13.08$  eV), suggesting that addition of  $(\text{CH}_3\text{O})_2\text{C}$  to  $\text{Me}_2\text{C}=\text{CMe}_2$  could be characterized as "electrophilic", if it occurred. In fact, even the smaller, dominant differential orbital energy is still quite large (as it also is for  $\text{Me}_2\text{C}=\text{CH}_2$  (13.0 eV) and *t*-MeCH=CHMe (12.9 eV)). Consequently, these three addition reactions do not derive enough transition-state stabilization to become energetically competitive with the alternative carbene reaction pathways which actually occur.<sup>3</sup>  
 (23) Postdoctoral Fellow on leave from the Technical University, Warsaw, Poland.

Robert A. Moss,\* Michal Fedorynski,<sup>23</sup> Wen-Chung Shieh  
 Wright and Rieman Laboratories, Department of Chemistry  
 Rutgers, The State University of New Jersey  
 New Brunswick, New Jersey 08903  
 Received April 30, 1979

## Carbene Rearrangements of 2-Vinylcyclobutylidene

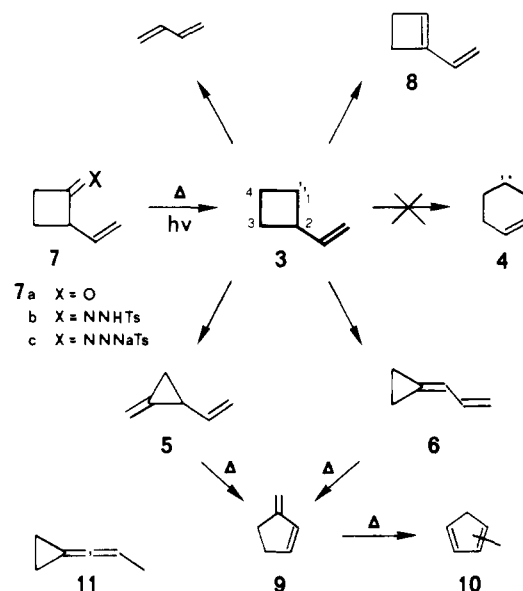
Sir:

Few carbene-carbene rearrangements<sup>1</sup> have been reported in which the divalent carbon retains its identity. With one exception<sup>2</sup> all known examples involve the conversion of vinylcyclopropylidenes **1** into cyclopentenylidenes **2**.<sup>3</sup>



We expected that 2-vinylcyclobutylidene (**3**) would undergo an analogous carbene-carbene rearrangement.<sup>4</sup> Furthermore, **3** makes possible the study of two competitive pathways in the cyclobutylidene-methylenecyclopropane rearrangement of an unsymmetrically monosubstituted cyclobutylidene. Cleavage of the C<sub>3</sub>-C<sub>4</sub> bond in **3** affords vinylmethylenecyclopropane (**5**),<sup>5</sup> whereas rupture of the C<sub>2</sub>-C<sub>3</sub> bond leads to allylidene-cyclopropane (**6**).<sup>6</sup> We find that the latter process predominates and that no carbene-carbene rearrangement (**3** → **4**) occurs.

2-Vinylcyclobutylidene (**3**) was generated either by decomposition of the dry 2-vinylcyclobutanone tosylhydrazone sodium salt (**7c**) in a flash pyrolysis system at 200 °C or by irradiation of **7c** in ethereal solution. The desired 2-vinylcyclobutanone (**7a**) was synthesized from 2-bromocyclobutanone<sup>7</sup>



via ketalization (yield, 77%) and then introduction of the vinyl group with vinylmagnesium bromide (61%) followed by de-ketalization (66%). Reaction of 2-vinylcyclobutanone (**7a**)<sup>8</sup> with tosylhydrazide gave the corresponding tosylhydrazone **7b** in 76% yield.

The product distributions recorded in Table I indicate that 1,2-hydrogen migration amounts to <5%, affording 1-vinylcyclobutene (**8**).<sup>9</sup> The parent cyclobutylidene produces 20% cyclobutene.<sup>10</sup> Decomposition (methods a, b) of **7c** yields 1,3-butadiene in trace amounts.

Depending on the method of generation, **6** and **5** are formed in ratios 53:1, 41:1, and 23:1, respectively (Table I). It should be taken into account, however, that 3-methylenecyclopentene (**9**),<sup>6,11</sup> as well as the methylcyclopentadienes (**10**),<sup>12</sup> stems from thermal rearrangement of **5**.<sup>13</sup> The yield of **9** decreased when a stream of nitrogen was passed through the pyrolysis system (b), and no secondary products were observed in the photolytic experiments (c). The available kinetic data<sup>14</sup> suggest that **6** does not rearrange significantly under the conditions of our pyrolysis studies. Thus, **6** and **5** may be actually produced in a ratio as low as 5:1 at 200 °C.

1,3- and 1,4-cyclohexadiene, the products expected from the carbene-carbene rearrangement **3** → **4**, were not detected among the compounds obtained.<sup>15</sup> This observation is in stark contrast with the formation of 84% cyclopentadiene from 2-vinylcyclopropylidene (**1**).

Assuming that the divalent carbon in its singlet state approaches sp<sup>2</sup> hybridization, thermochemical estimates show **3** to be considerably less strained (~10-13 kcal/mol) than **1**. Conformational effects and/or different methods of generation<sup>16</sup> may also be responsible for the divergent behavior of **1** and **3**.

We are currently exploring the chemistry of other vinylcyclobutylidenes and their tendency to undergo carbene-carbene rearrangements.

Acknowledgment is made to the Deutsche Forschungs-

Table I. Product Distribution from Decomposition of **7c**

method <sup>a</sup>	<b>6</b>	<b>5</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>7a</b>	<b>11</b> <sup>b</sup>	unidentified products	total isolated yield, %
a	74.1	1.4	3.8	12.8	0.4		5.4	2.1	63
b	85.3	2.1	3.9	4.9	0.4		1.9	1.5	71
c	60.7	2.6	1.3			28.9	5.3	1.2	4 <sup>c</sup>

<sup>a</sup> a, 200 °C, 10<sup>-3</sup> Torr; b, 200 °C, 0.9-0.7 Torr, N<sub>2</sub>; c, hv, 0 °C, ether, 6 h (125 W, Philips HPK). <sup>b</sup> The more NaH is used for the formation of the sodium salt **7c**, the more **11** is obtained in the reaction of **7c** (methods a, b, c). Under the reaction conditions **11** is not formed from **6**. <sup>c</sup> The difference in the total isolated yields (methods a, b vs. c) is due to the different methods (reaction times and workup procedures) applied.

gemeinschaft for support of this work. We thank Professor L. Skattebøl for permission to quote results prior to publication and Professor W. Kirmse for stimulating discussions.

## References and Notes

- (1) Jones, W. M.; Brinker, U. H. "Some Pericyclic Reactions of Carbenes" in "Pericyclic Reactions", Marchand, A. P., Lehr, R. E., Ed.; Academic Press: New York, 1977; Vol. I. Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353.
- (2) Baird, M. S.; Reese, C. B. *J. Chem. Soc., Chem. Commun.* **1972**, 523.
- (3) Skattebøl, L. *Tetrahedron* **1967**, *23*, 1107. Holm, K. H.; Skattebøl, L. *Tetrahedron Lett.* **1977**, 2347. Holm, K. H.; Skattebøl, L. *J. Am. Chem. Soc.* **1977**, *99*, 5480. Schoeller, W. W.; Brinker, U. H. *Ibid.* **1978**, *100*, 6012.
- (4) It has been shown that a vinylcyclopropylidene, whether generated from a dihalocyclopropane or from a diazocyclopropane precursor, gives nearly identical ratios of cyclopentadiene and vinylallene. Holm, K.; Skattebøl, L., unpublished results, reported at the EUACHEM Conference on Electron Deficient Intermediates, Geneva, Oct 9, 1978.
- (5) Billups, W. E.; Shields, T. C.; Chow, W. Y.; Deno, N. C. *J. Org. Chem.* **1972**, *37*, 3676. Arora, S.; Binger, P. *Synthesis* **1974**, 801.
- (6) Blome, H., Dissertation, Bochum, West Germany, 1973.
- (7) Ramirez, F.; Bellet, R. J. *J. Am. Chem. Soc.* **1954**, *76*, 491.
- (8) Satisfactory C, H analyses were obtained for all new compounds. The spectroscopical data are in agreement with the proposed structures. **7a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.55–3.20 (m, 4 H), 3.65–4.20 (m, 1 H), 4.95–6.20 (m, 3 H); IR (CCl<sub>4</sub>) 1791 (C=O) cm<sup>-1</sup>. **7b**: mp 89–90 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.50–3.20 (m, 4 H), 2.45 (s, 3 H), 3.55–4.05 (m, 1 H), 4.85–6.20 (m, 3 H), 7.20–8.00 (m, 4 H, AA'BB'). **11**: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 1.40 (d, 4 H, J = 3.5 Hz), 1.70 (d, 3 H, J = 7.0 Hz), 4.85–5.35 (m, 1 H, J = 7 Hz, J = 3.5 Hz); IR (neat) 2025 (C=C=C) cm<sup>-1</sup>.
- (9) Thummel, R. P.; Natakul, W. *J. Org. Chem.* **1977**, *42*, 300. 3-Vinylcyclobutene, the alternative product of a 1,2-hydrogen migration in **3**, may have been present in trace amounts.
- (10) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002. Kirmse, W. "Carbene Chemistry," 2nd ed.; Academic Press: New York, 1971.
- (11) Shields, T. C.; Billups, W. E.; Lepley, A. R. *J. Am. Chem. Soc.* **1968**, *90*, 4749. Billups, W. E.; Leavell, K. H.; Lewis, E. S.; Vanderpool, S. *Ibid.* **1973**, *95*, 8096.
- (12) Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Tetrahedron* **1963**, *19*, 1939. McLean, S.; Haynes, P. *Ibid.* **1965**, *21*, 2329.
- (13) The isomerization (**9** → **10**) under stationary pyrolysis conditions (300–350 °C) has been reported: Schmidt, T., Dissertation, Bochum, West Germany, 1972. Roth, W. R.; Schmidt, T.; Humbert, H. *Chem. Ber.* **1975**, *108*, 2171. Dewar, M. J. S.; Fonken, G. J.; Kirschner, S.; Minter, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 6750.
- (14) At 200 °C the rate constants of the reactions (**6** → **9**)<sup>6</sup> and (**5** → **9**)<sup>11</sup> are  $2.53 \times 10^{-4}$  and  $0.30 \text{ s}^{-1}$ , respectively. At this temperature with a contact time of 1.5 s, **6** virtually does not rearrange (~0.04%).
- (15) 1,3- as well as 1,4-cyclohexadiene is stable under the reaction conditions applied.
- (16) For the sole simple example of a Bamford–Stevens reaction of the sodium salt of the tosylhydrazone of 2,3-di-*tert*-butyl-cyclopropanone see: Greene, F. D.; Camp, R. L.; Abegg, V. P.; Pierson, G. O. *Tetrahedron Lett.* **1973**, 4091.

Udo H. Brinker,\* Lothar König  
Abteilung für Chemie der Ruhr-Universität  
4630 Bochum, West Germany  
Received March 19, 1979

## Absolute Configuration of (-)<sub>D</sub>-Tris(2,2'-bipyridine)cobalt(III)

Sir:

A direct determination of the absolute configuration of (-)<sub>D</sub>-tris(2,2'-bipyridine)cobalt(III) complex ((-)<sub>D</sub>-[Co(bpy)<sub>3</sub>]<sup>3+</sup>) presented here concludes a Δ configuration.

The absolute configuration of [Co(bpy)<sub>3</sub>]<sup>3+</sup> has been controversial. The CD spectrum of the enantiomer of this particular complex exhibits two CD bands of opposite signs in the bipyridine (π,π\*) absorption region at ~32 000 cm<sup>-1</sup>. An application of the exciton theory to the analysis of the CD bands of (-)<sub>D</sub>-[Co(bpy)<sub>3</sub>]<sup>3+</sup> yields a Δ configuration.<sup>1-5</sup> On the other hand, an alternative procedure, which should be well devised for the prediction of the absolute configuration of the coordinated ligands especially of those lacking the conjugated system, is based on an empirical analysis of both CD and absorption data of the (d,d\*) ligand-field band and its application in a traditional way assuming the CD intensity-dominant E state predicts a Λ configuration.<sup>6-8</sup> In fact, Hawkins and co-workers assigned a Λ configuration to (-)<sub>D</sub>-[Co(bpy)<sub>3</sub>]<sup>3+</sup>.<sup>7</sup>

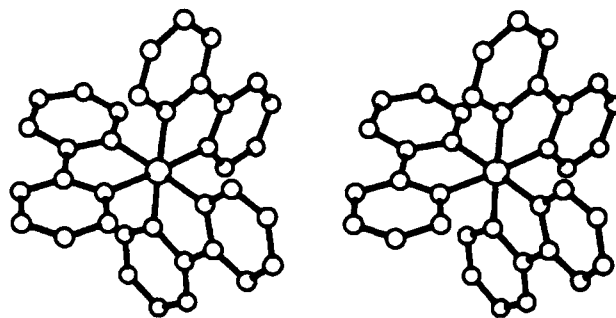


Figure 1. A stereoscopic view of (-)<sub>D</sub>-[Co(bpy)<sub>3</sub>]<sup>3+</sup>.

The enantiomer used in the earlier stage of the present work was prepared by chlorine oxidation of trisbipyridinecobalt(II) (+)<sub>D</sub>-bistartaratoantimonate(III) dispersed in carbon tetrachloride and deposited as crystals of (-)<sub>D</sub>-[Co(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O. Several trials with these perchlorate crystals did not give sufficient structural information because of the pseudosymmetry in the tetragonal unit cell. The anion was replaced by mixing the aqueous solution of the perchlorate complex with that of potassium hexacyanoferrate(III). The CD spectrum did not vary significantly before and after the anion exchange.

The prismatic crystals of (-)<sub>D</sub>-[Co(bpy)<sub>3</sub>][Fe(CN)<sub>6</sub>]·8H<sub>2</sub>O are triclinic with  $a = 12.174$  (3),  $b = 16.742$  (7),  $c = 10.651$  (3) Å;  $\alpha = 103.25$  (3),  $\beta = 104.09$  (2),  $\gamma = 94.71$  (3)°;  $V = 2027$  (1) Å<sup>3</sup>; space group *P*1. The density measured by flotation is  $1.46 \text{ g cm}^{-3}$ , whereas the calculated density is  $1.45 \text{ g cm}^{-3}$  if the crystal is assumed to have two formula units in the unit cell. Intensity data up to  $2\theta \leq 55^\circ$  were collected on a Rigaku four-circle diffractometer with Mo K $\alpha$  radiation monochromated by graphite. A total of 6348 independent reflections, ( $|F_o| \geq 3\sigma(|F_o|)$ ), were obtained. The structure was solved by the heavy-atom method and refined by the block-diagonal least squares, the final *R* being 0.076.

The absolute configuration of the (-)<sub>D</sub>-[Co(bpy)<sub>3</sub>]<sup>3+</sup> ion was assigned to Δ by the anomalous dispersion technique. Figure 1 is a stereoscopic view of the cation along its pseudo-three-fold axis. Average Co–N and N–Co–N are 1.932 Å and 83.2°, respectively. The other bond distances and angles are in good agreement with those of [Ni(bpy)<sub>3</sub>]<sup>2+</sup>.<sup>9,10</sup>

Corresponding to the Λ configuration of (+)<sub>D</sub>-[Co(bpy)<sub>3</sub>]<sup>3+</sup> determined in the present work, a Λ configuration has been suggested for (+)<sub>D</sub>-[Co(phenanthroline)<sub>3</sub>]<sup>3+</sup> ((+)<sub>D</sub>-[Co(phen)<sub>3</sub>]<sup>3+</sup>) on the basis of the sign of the optical rotation at the D line observed upon fast oxidation of the equilibrium enantiomeric mixture obtained in the presence of (*S*)-(-)<sub>D</sub>-malic acid.<sup>11</sup>

The absolute configuration supports the conclusion of exciton splitting analysis of the CD spectra in the lowest ligand (π,π\*) transition. The same theory also correctly predicts the Λ configurations of (+)<sub>D</sub>-[Ni(bpy)<sub>3</sub>]<sup>2+</sup>, (+)<sub>D</sub>-[Ni(phen)<sub>3</sub>]<sup>2+</sup>, and (-)<sub>D</sub>-[Fe(phen)<sub>3</sub>]<sup>2+</sup> which were already established by X-ray studies.<sup>10,12,13</sup> On the basis of the CD in the lowest ligand (π,π\*) transition, the absolute configurations of (-)<sub>D</sub>-[Fe(bpy)<sub>3</sub>]<sup>2+</sup> and (-)<sub>D</sub>-[Fe(phen)<sub>3</sub>]<sup>2+</sup> are assigned as the Λ configuration as well as those of the (+)<sub>D</sub> isomers of the ruthenium(II) and osmium(II) analogues, whereas the sign of the CD spectra in the visible charge-transfer band is not conserved. In the case of Ni(II) complexes, sufficient empirical relationships between configuration and the CD spectra in the lowest (d,d\*) ligand-field transition have not been obtained because of the difficulties of resolution of labile optical isomers.<sup>14</sup> It should be noted, however, that the sign of CD spectra in the lowest (d,d\*) transition (<sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> in *O<sub>h</sub>* symmetry) exhibited by the Λ isomers, (+)<sub>D</sub>-[Ni(bpy)<sub>3</sub>]<sup>2+</sup> and (+)<sub>D</sub>-[Ni(phen)<sub>3</sub>]<sup>2+</sup>, is consistently opposite to the sign observed in