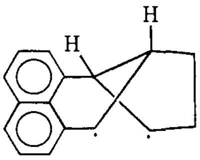
Table I. Pyrolysis of *cis*-Divinylacenaphthene

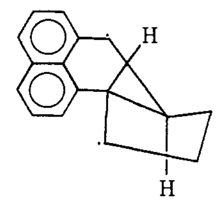
Starting material	Temp, °C	Residence time[a]	Relative amounts, %[b]				Material balance, %[c]
			4	**6**	**7**	**8**	
4	472	2.5	32	11	51	6	81
	439	2.5	44	2	54	0	
	418	2.5	71	1	28	0	88
	408	24	53	2	45	0	97
6	475	2.1	1	88	7	4	
7	472	2.5	30	5	55	10	96
	416	2.4	7	<0.5	93	0	95
	407	22	9	<0.5	90	1	102

[a] In arbitrary units, based on flow rate of nitrogen through the column. [b] Calculated from vpc peak areas (0.25 in., 10% FFAP column); the numbers appear to be reproducible to about 1%. [c] Using weight of starting material and vpc peak areas relative to that of acenaphthylene weighed into the collection trap.

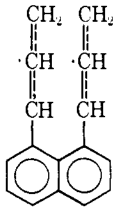
237 (4.55), 272 (3.69), 281 (3.88), 292 (3.97), 302 (3.82), 307 (3.54), 317 (3.07), 321 (3.01); mass spectrum *m/e* 206 (M$^+$, 85%), 165 (100)], which should be compared to those of the compound lacking the ethylene bridge, the major thermal[1] or photoproduct[7] from 1,8-divinylnaphthalene. We suggest that **7** most reasonably arises from 1,5 bonding in the mixture of **1** isomers formed from **4** by Cope rearrangement. Only relatively facile rotations are required to give diradical *cis*- and *trans*-**9** from **1** isomers, and 1,4-diradical cleavages would be expected to isomerize the **1** isomers readily. Only *cis*-**9** is geometrically capable of closure to **7**. Table I shows that **7**, which is a bicyclo[2.1.1]hexane derivative, is thermally stabler than **4**, which indicates that there must be a large π strain in **1**. Condensation of the pyrolysate from **4** directly on a liquid nitrogen cold finger did not give nmr detectable quantities of **1** isomers, indicating that they are considerably less thermodynamically stable than **4**.



cis-**9**



trans-**9**



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Product **8** was assigned as a hydrogen shift product derived from **9** because it clearly has a *peri*-naphthalene-type structure from its mass spectrum (*m/e* 206 (M$^+$, 100%), 205 (M$^+$ − H, 55), 165 (69)), and is formed in highest yield from the pyrolysis of **7**. Since it is not formed in detectable amounts from **4** at lower temperatures, this product has not been extensively investigated. *trans*-Divinylacenaphthene (**6**) was always a minor product, and it is not clear whether it is formed from "leakage" to diradical **10**, or whether it arises from Cope rearrangements of unstable **1** conformers. No **6** was detected by vpc in the Wittig products. The thermal stability of **6** is clearly greater than that of **4** or **7** on the basis of data given in Table I.

Some of the products reported by Mitchell and Sondheimer[8] from the reaction of **3** and the Wittig reagent from 1,8-bis(bromomethyl)naphthalene appear to be derivable by reactions similar to those reported here.

Further studies of the reported and similar reactions are in progress, to gain a clearer understanding of the thermodynamics and reaction pathways involved.

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Thermal Rearrangement of 1,8-Divinylnaphthalene

Sir:

Although it is a common photochemical reaction, the thermal cycloaddition of olefins to give cyclobutanes is quite rare in hydrocarbon systems. Low yields of cyclobutane derivatives have been observed from thermal reactions of styrene, butadiene, and a few other conjugated olefins,[1] and *cis,trans*-1,5- and 1,3-cyclooctadienes dimerize at the trans olefin groups in good yield.[2]

The only intramolecular cases of such a reaction we have been able to find were reported by Wittig and coworkers,[3a] who found that heating one isomer of 1,2,-3,4,7,8,9,10-tetrabenzocyclododecahexaene to 180° gave a bis(biphenylene)cyclobutane, which cleaved to phenanthrene at 240°, and by Mitchell and Sondheimer,[3b] who report a similar example in an 11-membered ring case. Stiles and Burckhardt[4] studied the thermal isomerization of 3,4-diphenyl-1,2,5,6-dibenzocyclooctatetraene to the 3,7-diphenyl isomer, where a cyclobutane intermediate is definitely implicated, but the cyclobutane was not detected, even in low-temperature photolyses.

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(7) J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**, 724 (1971).

(8) R. H. Mitchell and F. Sondheimer, *ibid.*, 90, 530 (1968).

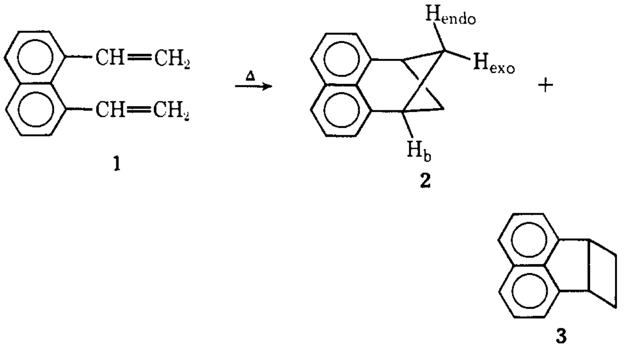
(1) (a) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); (b) P. D. Bartlett and K. E. Schueller, *J. Amer. Chem. Soc.*, **90**, 6061 (1968).

(2) (a) A. C. Cope, C. F. Howell, and A. K. Knowles, *ibid.*, **84**, 3190 (1962); (b) K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4357, 4723 (1967); (c) C. L. Osborn, D. J. Trecker, A. Padway, W. Kohen, and J. Masarachia, *ibid.*, 4653 (1970).

(3) (a) G. Wittig, G. Koenig, and K. Claus, *Justus Liebigs Ann. Chem.*, **593**, 127 (1955); (b) R. H. Mitchell and F. Sondheimer, *Tetrahedron Lett.*, 2873 (1968).

(4) M. Stiles and U. Burckhardt, *J. Amer. Chem. Soc.*, **86**, 3396 (1964).

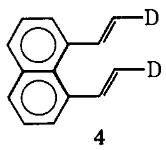
We wish to report the efficient thermal conversion of 1,8-divinylnaphthalene (**1**)[5] to intramolecular 2 + 2 adducts. Pyrolysis[6] of **1** at 425° converted it completely to a 4 : 1 mixture of **2** and **3**, which were identified by comparison with samples prepared by the photolysis of **1**;[7] other products were not detected.



We suggest that the driving force for this unusual conversion lies in the considerable strain caused by forcing the π clouds of the *peri*-vinyl substituents of **1** into each other, which we shall refer to as π strain. The distance between C_1 and C_8 in naphthalene is 2.50 Å, and that between the methyl groups of 3-bromo-1,8-dimethylnaphthalene is 2.92 Å,[8] while twice the van der Waal's radius for end-on approach of sp^2-hybridized carbons (which we approximate as twice the interplanar distance of graphite[9]) is about 3.4 Å. Although the vinyl groups of **1** are free to rotate to minimize the vinyl–vinyl interaction, the formation of **2** and **3** upon heating **1** is a definite indication that there is considerable π strain in **1**.

The question of possible stereochemical preferences for the intramolecular cyclization of **1** is of obvious interest, especially since the *cis,trans*-cyclooctadiene dimerization has been shown to occur with the geometry predicted for the allowed 2s + 2a cycloaddition.[2b] The geometry necessary for a concerted addition could only be conceivably approximated for the reaction leading to **2**, and testing the stereochemistry requires stereospecific labeling of both CH$_2$ groups. We prepared *trans,trans*-**1**-d_2 (**4**) highly stereospecifically by the dicyclohexylborane reduction[10] of the diacetylene **5**,[11] followed by work-up with deuterioacetic acid, although both the yield (21%) and per cent deuteration were disappointingly low. Our sample of deuterated **1** contained 58% d_2, 34% d_1, and 8% d_0 (by mass spectroscopy). The deuterium present was completely trans to the aromatic ring (to nmr accuracy) as expected from the method of synthesis.

The stereochemistry of deuterium in deuterated **2** is obtainable from the nmr spectrum of H_b, which is a triplet in unlabeled **2** ($J_{\text{b-exo}}$ = 5.4, $J_{\text{b-endo}}$ = 0 Hz[7]). Complete randomization of deuterium in our sample of deuterated **1** would give a 1:2.3:3.5 quintet for H_b, while a concerted 2s + 2a addition would give only *exo,endo*-**2**-d_2 from **4**; with the isotopic mixture employed, a 1:6:2 quintet would be observed for H_b.[12] Pyrolysis of our sample at 350° gave 67% recovered divinylnaphthalene, in which about 10% of the vinyl groups were cis deuterated (determined by nmr). Neither **2** nor **3** pyrolyzes to give **1** under these conditions. This result indicates that although stereochemistry is partly lost during the cyclization reaction, as expected for a diradical pathway, complete randomization of deuterium is not occurring. Different stereochemistries in the **2** formed would occur from the two rotamers of **4**, as shown below.



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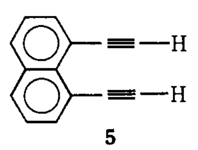

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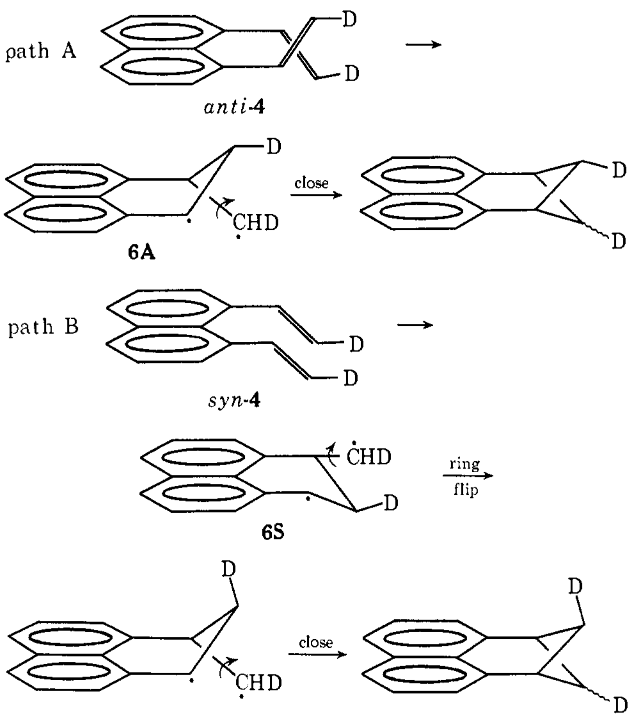

Assuming that rotation about the single bonds of **6A** and **6S** is rapid compared to ring closure to **2**, path A would result in a 1:6.6:9.0 quintet, and path B would give a 1 : 1.2 : 2.0 quintet (using our mixture of deuterated material, but not corrected for isomerization of starting material). We observed a 1 : 1.7 : 2.8 quintet (deuterium decoupled), showing that path B predominates over path A. Since *anti*-**4** is doubtless the preferred conformer,[6] more rapid diradical formation from the most strained conformer is not unreasonable.

The stereochemical evidence is consistent with the formation of **2** from **1** proceeding through diradicals.

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(5) Prepared by the method of J. K. Stille and R. T. Foster, *J. Org. Chem.*, **28**, 2703 (1963).

(6) By sweeping with nitrogen, through a heated column packed with ¼-in. glass helices.

(7) J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**, 724 (1971).

(8) M. B. Jameson and B. R. Penfold, *J. Chem. Soc.*, 528 (1965).

(9) J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, p 713.

(10) G. Zweifel, G. M. Clark, and N. L. Polston, *J. Amer. Chem. Soc.*, **93**, 3395 (1971).

(11) R. H. Mitchell and Sondheimer, *Tetrahedron*, **24**, 1397 (1968).

(12) These calculations for the appearance of the H_b pattern ignore isotope effects, and only the outer, intermediate, and center line intensities are listed. For a concerted 2s + 2a reaction, **1**-d_2 (58%) gives only *exo,endo*-**2**-d_2, resulting in an H_b doublet, while **1**-d_1 (34%) gives an equal mixture of *exo*- and *endo*-**2**-d_1, resulting in a doublet and triplet, respectively. Since **1**-d_0 (8%) can give only a triplet, 58 + 17 = 75% of the **2** formed would have a doublet for H_b, and 17 + 8 = 25% a triplet, resulting in the 1:6:2:6:1 pattern for H_b which is listed in the text.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, the National Science Foundation for major instrument grants used in purchasing spectroscopic equipment, and Mr. David Hillenbrand for running the deuterium-decoupled nmr spectra.[13]

(13) Note Added in Proof. We thank Professor Meinwald for communicating his results in this area prior to publication.

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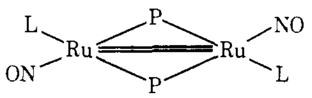
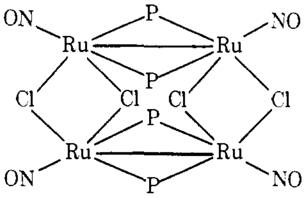
Nitrosyls and Metal–Metal Bonding in μ-Diphenylphosphido Ruthenium Clusters

Sir:

Metal nitrosyl cluster compounds are intriguing systems because of the current interest in metal–nitrosyl bonding[1–3] and the potential applicability of these systems as homogeneous multicenter catalysts.[4,5] Nitrosyl, unlike carbonyl, can coordinate to a metal ion in one of several ways,[1–3] and it has been suggested[6] that in doing so the NO ligand can activate the metal ion by alternately withdrawing and donating an electron pair. In nitrosyl clusters, this feature is coupled with the presence of more than one metal center and consequent metal–metal bonding which has attracted attention during recent years.[7–10] We report herein the synthesis and structure determination of two novel ruthenium nitrosyl cluster compounds, **1** and **2**, in which the mode of nitrosyl coordination changes from linear to slightly bent and the degree of metal–metal bonding differs significantly.



1, L = $P(CH_3)(C_6H_5)_2$; P = $P(C_6H_5)_2$



2, P = $P(C_6H_5)_2$

Complex **1** was initially obtained in small amounts from a recrystallization of $RuH(NO)(P(CH_3)(C_6H_5)_2)_3$[11] using excess phosphine apparently contaminated with $HP(C_6H_5)_2$. The structure determination of **1**, outlined below, led us to devise a more rational synthesis of the complex which also yielded several other products including **2**. The synthesis consists of the addition of a benzene solution of $RuCl_3(NO)(P(CH_3)(C_6H_5)_2)_2$ and $HP(C_6H_5)_2$ (1 : 1) to a stirred Zn|Cu couple followed by filtration, evaporation, and separation of products. To date, difficulties in the last step have produced **1** and **2** in low yield only. Crystals of **2** for X-ray work were grown from a benzene–methanol solution.

Unit Cell and Space Group Data. **1** has a unit cell with dimensions a = 13.12 (1), b = 12.95 (1), c = 15.94 (2) Å; β = 120.2 (1)°; V = 2341 Å^3; space group $P2_1/c$; ρ_{exptl} = 1.46 (2) g/cm^3; ρ_{calcd} = 1.47 g/cm^3; Z = 2. **2** has a unit cell of dimensions a = 15.92 (1), b = 12.49 (1), c = 26.16 (1) Å; V = 5200 Å^3; space group, $Fmmm$; ρ_{exptl} = 1.79 (2) g/cm^3; ρ_{calcd} = 1.80 g/cm^3; Z = 4.

Intensity data for both complexes were collected by the θ–2θ scan technique using Zr-filtered Mo Kα radiation and pulse height analysis. Intensities within the angular ranges $5° \leqslant 2\theta_{\text{Mo}} \leqslant 50°$ for **1** and $5° \leqslant 2\theta_{\text{Mo}} \leqslant 55°$ for **2** were measured thereby yielding 1659 reflections above 3σ for **1** and 1415 above 2σ for **2**. Both structures were solved by standard Patterson and Fourier methods and were refined by a least-squares procedure in which individual atoms were assigned anisotropic thermal parameters. In **1**, the phenyl rings were treated as rigid groups.[12,13] The refinements of the two structures have converged to conventional and weighted R factors of 0.054 and 0.065 for **1** and 0.049 and 0.073 for **2**.

The structures of the two complexes are illustrated in Figures 1 and 2, respectively, with the important bond distances and angles summarized in the figure captions. **1** is a centrosymmetric binuclear complex with the ruthenium atoms bridged by diphenylphosphido groups and the coordination geometry distorted tetrahedral. The nitrosyl ligand is coordinated in an essentially linear manner although the Ru–N–O bond angle of 174.1 (9)° deviates significantly from 180°. The Ru–N distance of 1.697 (12) Å is slightly shorter than other observed Ru–linear nitrosyl bond lengths[1] and is indicative of a strong π-backbonding interaction as would be expected for linearly bonded nitrosyl. The dihedral angle of 85.6 (2)° between the planes defined by Ru,P_1,P_1' and Ru,P_2,N (see Figure 1) is in accord with that expected for a slightly distorted tetrahedron. One of the most striking features of the structure is the occurrence of a strong metal–metal bond (*vide infra*) as evidenced by the short Ru–Ru distance of 2.629 (2) Å and the Ru–P–Ru bond angle of 69.7 (1)°.

Complex **2** is a tetranuclear system which is crystallographically required to have *mmm* (D_{2h}) symmetry. The four Ru atoms of the cluster form a rectangular array in which opposite pairs of the metal atoms are bonded covalently with a Ru–Ru distance of 2.787 (2) Å and the pairs are separated by a nonbonding Ru–Ru distance of 3.672 (1) Å (see Figure 2). The metal–metal bonded ruthenium atoms are bridged by diphenylphosphido groups as in **1** while the nonbonding ruthenium atoms are bridged by chlorines. The coordination

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(1) C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971); *Inorg. Chem.*, **11**, 1088, 1094 (1972), and references cited therein.

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(3) Abstracts of the American Crystallographic Association Meeting, Albuquerque, N. Mex., April 3–7, 1972, further underscore the structural interest in these systems. See C. S. Pratt, *et al.*, Abstract H3; J. H. Enemark and R. D. Feltham, Abstract H4; and R. M. Kirchner and J. A. Ibers, Abstract H6.

(4) J. Norton, D. Valentine, Jr., and J. P. Collman, *J. Amer. Chem. Soc.*, **91**, 7537 (1969).

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(8) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).

(9) F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969).

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(11) S. T. Wilson and J. A. Osborn, *ibid.*, **93**, 3068 (1971).

(12) S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(13) R. J. Doedens in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 198.