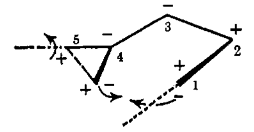
Acknowledgments. The authors thank Dr. W. T. Pace for nmr results and Mr. C. O. Allen for ultraviolet spectra.

[12] It is possible, using inversion[6] at the atom which breaks and makes a ring σ bond, to formulate a concerted reaction involving disrotation at the *exo* position in the initial and final states.



π AO sign					
5	4	3	2	1	atom
	–	–	+	+	reactant
+	0	–	0	+	intermediate
+	+	–	–		product

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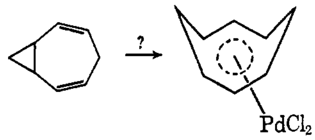
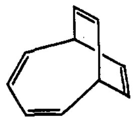
The Rearrangement of Bullvalene–Palladium Chloride Complex

Sir:

Numerous 1,4- and 1,5-dienes form palladium chloride π complexes in which the chlorine ligands remain attached to palladium.[1] On the other hand, conjugated acyclic dienes[2a,b] and vinylcyclopropanes[2c] react with palladium chloride to form π-allyl complexes in which a chlorine atom is transferred to carbon. In the case of homotropilidenes, both types of behavior are conceivable, but in addition there exists the intriguing possibility that all six homotropilidene π electrons can interact with palladium to yield a pseudoarene complex such as **1**. During our efforts to determine the structure of homotropilidene–palladium chloride complexes we have encountered a facile rearrangement of bullvalene to bicyclo[4.2.2]deca-2,4,7,9-tetraene (**2**), which is the subject of this communication.[3]



1

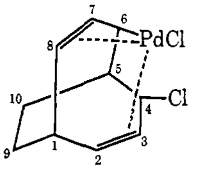


2

Treatment of bullvalene[4] with 1 equiv of bis(benzonitrile)palladium dichloride[5] at room temperature results in rapid precipitation of a dark, amorphous solid with the expected displacement of benzonitrile. After filtration, the solid is treated with aqueous pyridine or dimethyl sulfoxide to liberate the complexed hydrocarbons. Analysis of the products by glpc shows a single major component, isolated in 60% yield, which is identical with bicyclo[4.2.2]deca-2,4,7,9-tetraene (**2**).[6] Small amounts of naphthalene and *cis*-9,10-dihydronaphthalene[7] are also present, as shown by spectral and glpc comparison with authentic samples, but no trace of bullvalene can be detected. However, the rearrangement can be suppressed completely by repeating the experiment at −40°. Under these conditions, an orange complex (**3**) is formed in quantitative yield, and treatment of **3** with dimethyl sulfoxide results in recovery of 95% of the starting bullvalene. The crystalline bullvalene–palladium chloride complex **3** is stable for short periods at 0°, but all efforts to prepare solutions of **3** resulted in rearrangement.

The conversion of bullvalene to bicyclo[4.2.2]deca-2,4,7,9-tetraene also takes place catalytically. This variation constitutes a practical synthesis of **2**, since at low conversion **2** is the sole product. With longer reaction times and more catalyst, naphthalene and 9,10-dihydronaphthalene can be detected.[8] Control experiments show that these side products are also formed from purified **2**, thereby substantiating the view that **2** is the *sole initial* rearrangement product of bullvalene–palladium chloride complex **3**.

Since the complex **3** is too unstable for spectral studies, the palladium chloride complex **4**[9] of dihydrobullvalene[4] was prepared as a model for **3**. The nmr spectrum of **4** (Table I) is in accord with an unsymmetrical structure in which the cyclopropane ring is no longer intact,[2c] as shown by the number of low-field hydrogens. Of several isomeric structures which are possible, only **4** is consistent with chemical shift[10,11] and



4

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[1] M. Dub, "Organometallic Compounds," Vol. 1, 2nd ed, Springer-Verlag Inc., New York, N. Y., 1966, pp 865–866; H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967); E. E. van Tamelen and D. Carty, *J. Am. Chem. Soc.*, **89**, 3922 (1967); H. Frye, E. Kuljian, and J. Viebrock, *Inorg. Nucl. Chem. Letters*, 2, 119 (1966); J. C. Trebellas, J. R. Olechowski, and H. B. Jonassen, *J. Organometal. Chem.* (Amsterdam), **6**, 412 (1966).

[2] (a) B. L. Shaw, *Chem. Ind.* (London), 1190 (1962); (b) M. Donati and F. Conti, *Tetrahedron Letters*, 1219 (1966); (c) J. A. Braatz and A. D. Ketley, *J. Organometal. Chem.* (Amsterdam), **9**, P5 (1967); T. Shono, T. Yoshimura, Y. Matsumura, and R. Oda, *J. Org. Chem.*, **33**, 876 (1968).

[3] A similar rearrangement appears to occur upon treatment of bullvalene with iron carbonyl: G. N. Schrauzer, P. Glockner, and R. Merenyi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 509 (1964). Related findings are described by U. Kruerke, *ibid.*, **6**, 79 (1967), and by G. N. Schrauzer and P. Glockner, *J. Am. Chem. Soc.*, **90**, 2800 (1968). Stable silver complexes of bullvalene have been prepared: A. Allerhand and H. S. Gutowski, *ibid.*, **87**, 4092 (1965); J. S. McKechnie, M. G. Newton, and I. C. Paul, *ibid.*, **89**, 4819 (1967).

[4] G. Schröder, *Ber.*, **97**, 3140 (1964).

[5] M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, 60, 882 (1938).

[6] M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967). We are grateful to Professor Jones for providing spectra of 2.

[7] W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 23, 3943 (1967).

[8] The following procedure is useful for the preparation of bicyclo[4.2.2]decatetraene: Bullvalene (2.26 g) in dry chloroform (30 ml) is refluxed for 3 hr with bis(benzonitrile)palladium dichloride (0.07 g, 0.02 equiv). Most of the chloroform is then distilled off using a Vigreux column, and the residue is separated by preparative tlc on silica gel (100 cm × 20 cm, 1.5 mm layer) with hexane to afford starting bullvalene (0.36 g, R_f 0.3), 2 (1.5 g, R_f 0.45), and a zone containing naphthalene and 9,10-dihydronaphthalene in a 4:1 ratio (0.3 g, R_f 0.55).

[9] Dihydrobullvalene can be recovered from 4 upon treatment with cold pyridine, but solutions of the complex decompose gradually at room temperature.

[10] The chemical shift (τ 4.2) of H$_8$ is at least 1 ppm too low for consideration of a π-allyl structure for 4: K. C. Ramey and G. L. Statton, *J. Am. Chem. Soc.*, **88**, 4387 (1966); R. Hüttel, H. Christ, and K. Herzog, *Ber.*, **97**, 2710 (1964).

[11] The nmr spectrum of 4 is reversibly temperature dependent below the decomposition point of 60°. The chemical shifts of H$_6$ and H$_8$ gradually converge (H$_6$, τ 7.0 and H$_8$, τ 3.9 at −50°; H$_6$, τ 5.5 and H$_8$, τ 4.3 at 60°), indicating increased bonding between C$_8$ and palladium at higher temperatures.

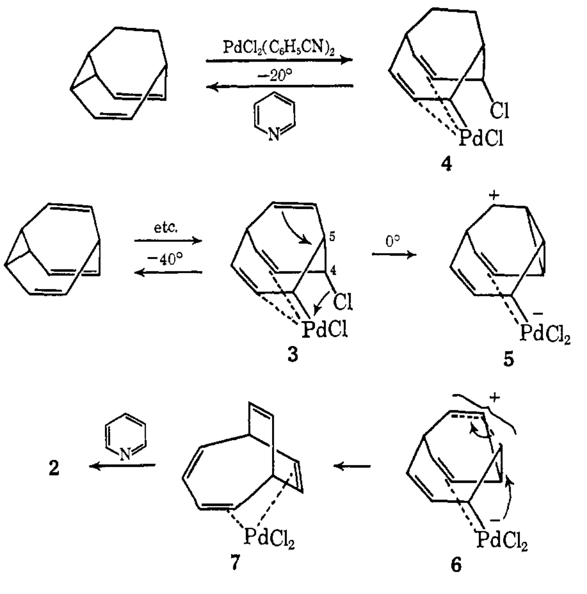
spin–spin coupling parameters. By analogy, the bullvalene complex **3** is tentatively assigned a similar allylpalladium structure.

Table I. Nmr Spectrum (100 Mc) of Dihydrobullvalene–Palladium Chloride Complex **4** at 10° in $CDCl_3$

Chemical shift, τ	Integral	Assignment	Coupling constants (by multiple spin decoupling)
4.0–4.4[a]	3	H_2, H_3, H_8	Complex multiplet
4.71	1	H_7	Triplet, $J_{6,7} = J_{7,8} = 8.0$ cps
4.82	1	H_4	Doublet of doublets, $J_{3,4} = 3.8$ cps, $J_{4,5} = 6.7$ cps
5.79	1	H_6	Doublet of doublets, $J_{6,7} = 8.0$ cps, $J_{5,6} = 8.9$ cps
6.84	1	H_1	Multiplet, $J_{1,2} = J_{1,8} = 8.0$ cps, $J_{1,9} = 3.0$ cps
7.6–8.6	5	H_5, H_9, H_{10}	Complex multiplet

[a] Olefinic hydrogens are slightly deshielded in π-olefin–palladium complexes when compared to the parent hydrocarbons: J. K. Stille and R. A. Morgan, *J. Am. Chem Soc.*, **88**, 5135 (1966); H. Takahashi and J. Tsuji, *ibid.*, **90**, 2387 (1968).

The rearrangement of bullvalene–palladium chloride complex **3** is a novel variant of the familiar homoallyl–cyclopropylcarbinyl interconversion. Ordinarily, it is expected that displacement of the C_4 chloride will be assisted by the bridging double bond to form a cyclopropylcarbinyl structure, **5**.[12] However, the remarkable ease of the rearrangement is best explained if vacant palladium coordination sites also assist the departure of the chloride ion, an effect which resembles silver ion induced polarization of carbon–halogen bonds.[16] The interaction[17] between palladium and the C_4 chloride is further apparent in the facile conversion of **3** and **4** to bullvalene and dihydrobullvalene,[9] respectively, upon treatment with coordinating solvents at −20°. Since **5** may equilibrate with its homoallyl isomer **6**, the occupied palladium d orbitals can now bond to the electron-deficient C_5, resulting in the formation of a π complex (**7**) of bicyclo[4.2.2.]deca-2,4,7,9-tetraene to complete the rearrangement.



The thermal behavior of other homotropilidene–palladium chloride complexes is under investigation and will be described in a future publication.

Acknowledgments. We are grateful to the Research Corporation for financial support and to Badische Anilin und Sodafabrik for a gift of cyclooctatetraene.

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(12) A substituted bicyclo[3.2.1]octadienyl bromide rearranges to its cyclopropylcarbinyl isomer at 80°;[13] a related chloride is stable up to 180°.[14] Bicyclo[3.2.2]nonatrienyl carbonium ion also affords cyclopropylcarbinyl products.[15] To our knowledge, no work has been done with bicyclo[3.3.2]decatrienyl derivatives which might be analogous to complex **3**.

(13) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

(14) D. C. F. Law and S. W. Tobey, *J. Am. Chem. Soc.*, **90**, 2376 (1968).

(15) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967).

(16) N. Kornblum and D. E. Hardies, *ibid.*, **88**, 1707 (1966).

(17) Other examples of the palladium(II)-induced polarization of a carbon–chlorine bond include carbonylation[18] and alcoholysis[2a,19] of the butadiene–palladium chloride complex.

(18) J. Tsuji and S. Hosaka, *J. Am. Chem. Soc.*, **87**, 4075 (1965).

(19) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963).

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On the Stereochemistry of Quaternization of Pseudotropine[1]

Sir:

More than 15 years ago, Fodor, Koczka, and Lestyán assigned structure III to the major quaternization product of pseudotropine (I) and ethyl iodoacetate and structure IV to the major product of N-ethoxycarbonylnorpseudotropine (II) and methyl iodide.[2] These assignments were based on the observations that the latter product, but not the former, could be converted in poor yield to a substance that had an elemental analysis and ir spectrum consistent with a lactone structure. If the structures are as proposed, then the major quaternization products are formed from the less stable amine conformers.[3,4] In contrast, recent studies[7,8b,9] indicate that, for most alkyl-substituted piperidines, the major quaternization products from reactions with alkyl iodides or sulfonates are formed from the more stable amine conformer. We describe here results that lead us to conclude that the actual structures of these quater-

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(1) Supported in part by Grant CA-05528 from the National Cancer Institute of the Public Health Service.

(2) G. Fodor, K. Koczka, and J. Lestyán, *Magy. Kem. Folyoir.*, **59**, 243 (1953); *J. Chem. Soc.*, 1411 (1956).

(3) (a) G. L. Closs, *J. Amer. Chem. Soc.*, **81**, 5456 (1959); and (b) G. Fodor, *Alkaloids*, **9**, 269 (1967).

(4) The results of an X-ray diffraction study of "N-ethylnortropine methobromide"[5,6] seem to indicate that the major quaternization product of tropine and ethyl iodide is formed from the less stable amine conformer. Also, very recently, Fodor, Medina, and Mandava,[6] on the basis of nmr data, have concluded that the major products of quaternizations of tropine and pseudotropine with deuteriomethyl iodide are formed from the *more* stable amine conformers, but that the major products with ethyl iodide are formed from the less stable amine conformers. Because of other work,[7-9] we find it difficult to accept this latter conclusion.

(5) C. H. McGillavry and G. Fodor, *J. Chem. Soc.*, 597 (1964).

(6) G. Fodor, J. D. Medina, and N. Mandava, *Chem. Commun.*, 581 (1968).

(7) H. O. House, B. A. Tefertiller, and C. G. Pitt, *J. Org. Chem.*, **31**, 1073 (1966).

(8) (a) A. T. Bottini, B. F. Dowden, and R. L. VanEtten, *J. Amer. Chem. Soc.*, **88**, 3250 (1965); (b) A. T. Bottini and M. K. O'Rell, *Tetrahedron Lett.*, 423 (1967).