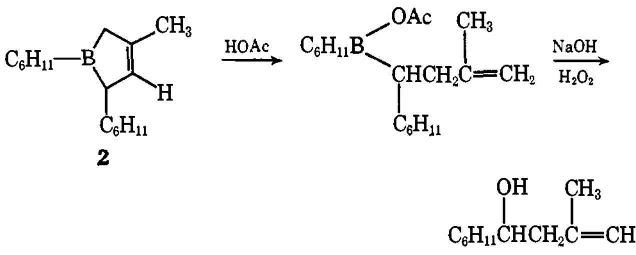
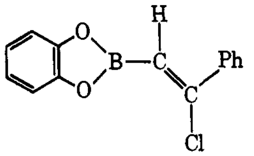
Protonolysis of the boracyclopentene **2** with acetic acid followed by oxidation afforded 1-cyclohexyl-3-methyl-3-buten-1-ol (**4**) in 71% isolated yield.[6] The observed migration of the double bond in this reaction presumably takes place during the protonolysis of the organoborane.[7] It should also be noted that the double bond migrates exclusively in one direction.



2

4

In view of the reported stability to ultraviolet irradiation of the vinylboranes **5**[8] and **6**[9], the deep-seated rearrangement of the dienylborane **1** is rather remarkable. Although the mechanistic details of the photoreaction are not yet known, it is apparent that both cyclization and migration of the cyclohexyl moiety from boron to the adjacent carbon must occur subsequently to an excited-state trans–cis isomerization. Whether cyclization and alkyl migration proceed in a concerted[10] or sequential[12] manner is a question we are currently attempting to answer.



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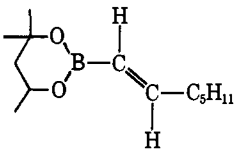

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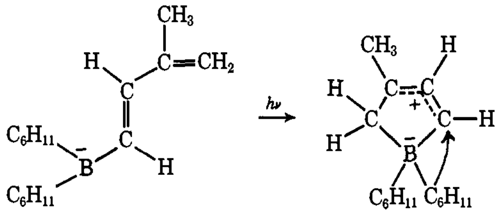

This discovery that dienylboranes undergo photocyclization opens a new area of synthetic and theoretical interest. We are continuing to explore the full scope of the photochemistry of vinyl- and dienylboranes.

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G. M. Clark, K. G. Hancock, G. Zweifel*
Department of Chemistry, University of California, Davis
Davis, California 95616

Received November 21, 1970

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[6] Structure **4** was established from spectral data and elemental analysis and by direct synthesis from cyclohexanecarboxaldehyde and isobutenylmagnesium chloride.

[7] Migration of the double bond on hydrolysis of allylic boron derivatives has been previously reported: B. M. Mikhailov and A. Ya. Bezmenov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 904 (1965); H. C. Brown and H. Nambu, *J. Amer. Chem. Soc.*, **92**, 1761 (1970).

[8] M. Lappert and B. Prokai, *J. Organometal. Chem.*, **1**, 384 (1966).

[9] W. G. Woods and P. L. Strong, *J. Amer. Chem. Soc.*, **88**, 4667 (1966).

[10] Concerted cyclization–migration would thus be the boron (uncoordinated) version of the $[\pi 4 + \sigma 2]$ cycloaddition–sigmatropic shift of a pentadienyl cation.[11]

[11] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

[12] Cyclization (an allowed four-electron, excited-state disrotatory closure) may equally well be followed by migration of the cyclohexyl moiety from boron to carbon. The favored photochemical reaction pathway in tetraarylboronate complexes, for example, appears to involve aryl migration from tetracoordinate boron to the electron-deficient carbon.[13]

[13] J. L. R. Williams, J. C. Doty, P. J. Grisdale, T. H. Regan, G. P. Happ, and D. P. Maier, *J. Amer. Chem. Soc.*, **90**, 53 (1968), and references therein.

Oxidation Product of Bis(diphenylglyoximato)palladium(II) with Iodine[1]

Sir:

Recently the results of magnetic and X-ray studies on compounds of the type $M(dpg)_2X$, where $X = I$ or Br, $M =$ Ni(II) or Pd(II), and dpg stands for the anion diphenylglyoxime, were reported.[2] Our investigations on the electrical conductivity of solid transition metal complexes prompted us to prepare single crystals of the cited compounds using the earlier described procedures.[2,3a] In the case of $Pd(dpg)_2I$ greenish needles with a remarkable metallic luster were obtained, in contradiction to the earlier statement of black reaction products.[2a,3] There is one other striking difference between Soderberg's findings and ours. A pure sample of the palladium–iodine complex did not show any esr absorptions even at liquid nitrogen temperature. The only observed effect during the study of the esr properties was a strong reduction of the cavity Q value by inserting the sample. This loss in reflected energy resembles in all respects the observations made after inserting finely dispersed metals into a cavity. This fact suggests in our opinion the presence of mobile conduction electrons in the solid complex $Pd(dpg)_2I$.

The formerly observed esr signals for this reason cannot be due to the proposed charge-transfer complex involving iodine and phenyl groups.[2a] The small amount of paramagnetic species found by Soderberg in $Pd(dpg)_2I$, and which always occurs in $Ni(dpg)_2I$, is, in our opinion, caused by lattice defects, where distinct paramagnetic, formally nickel(III) complex units cannot pair their free spins with neighboring ions. This explanation is supported by the earlier observed g values and their considerable anisotropy.[2a]

The results of far-ir[4] and uv investigations together with the above-mentioned physical properties led us to propose for these complexes a structure similar to those found in the iodine–starch compounds and related

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[1] The investigation was supported by Deutsche Forschungsgemeinschaft, Bad Godesberg.

[2] (a) A. S. Foust and R. H. Soderberg, *J. Amer. Chem. Soc.*, **89**, 5507 (1967). (b) One of the reviewers kindly pointed out that neither this paper nor the earlier ones on this subject[2a,3] acknowledge the original preparation of these complexes by L. E. Edelman, *ibid.*, **72**, 5765 (1950). This work is remarkable at least in one respect, since Edelman emphasized for the first time the bronze, metallic sheen of the crystallized $Ni(dpg)_2I$.

[3] (a) M. Simek, *Collect. Czech. Chem. Commun.*, **27**, 337 (1962). (b) The olive green sheen of crystallized samples disappears after grinding the compound, giving rise to a dark brown, almost black, color.

[4] No I–I stretching vibration, which is typical for iodine charge-transfer complexes in the region of 200 cm^{-1}, and no metal–halogen vibration, typical for other oxidized bis(glyoximato)palladium(II) compounds, can be found.

adducts of triiodide, I_3^-, to linear polymer matrices. The properties and structures of these species were thoroughly discussed during the last years.[5–8] In Pd(dpg)$_2$I the matrix is built by the regularly arranged phenyl groups. The binding of I_3^- to this linear array seems to be much stronger than in the iodine–starch species. This is caused by the resulting positive charge on the linear chain of palladium ions—leading to a shortened palladium–palladium distance—and the negative charge of the linear I_3^- chain. The visible spectrum of the solid palladium complex resembles in all respects those found for the mentioned triiodide compounds.

There is one analytical proof of the suggested structure. The amounts of iodine and iodide can be determined by dissolving the complex Pd(dpg)$_2$I in hydrochloric acid. In this way the compound is decomposed without redox reactions. It is found by using copper(II) and thiosulfate in the conventional titrimetric method that these species actually contain iodide and that elementary iodine molecules and iodide ions are present in almost the same amount. This means the stoichiometry of I_3^- units can be established analytically.

(5) R. Bersohn and I. Isenberg, *J. Chem. Phys.*, **35**, 1640 (1961).
(6) G. M. Olson and R. A. Berg, *ibid.*, **48**, 1426 (1968).
(7) I. Isenberg and R. Bersohn, *ibid.*, **48**, 1427 (1968).
(8) P. K. Rawlings and F. W. Schneider, *ibid.*, **52**, 946 (1970).

Heimo J. Keller, K. Seibold
Anorganisch-chemisches Laboratorium der Technischen Universität
Munich, Germany

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Concerning Contrasting Effects of Base Structure on Hydrogen-Bonded Ion-Pair and Hydrogen-Bonded Complex Formation[1]

Sir:

We have utilized the fluorine nuclear magnetic resonance (F nmr) shift, Δ, of the *p*-fluorobenzenesulfonate ion, measured in the polar aprotic solvent CH_2Cl_2, to scale (approximately) the electron densities with which the proton interacts in the conjugate acids of general bases (BH^+). The approximate scale of electron densities in general bases (B), at the site of hydrogen-bonded complex formation, has been previously obtained using the F nmr shifts of *p*-fluorophenol in CCl_4 solution.[2] The assumption is made that, in either our series of hydrogen-bonded ion pairs ($A^- \cdots {}^+HB$)[3] with *p*-$FC_6H_4SO_3^-$ or the corresponding series of hydrogen-bonded complexes ($AH \cdots B$)[3] with *p*-F_6H_4OH, the hydrogen bonding does not appreciably polarize or distort the scales of electron densities applicable for free BH^+ or B, respectively. This assumption, which is necessarily approximate, is based upon the relatively weak strength of the hydrogen-bonding interaction compared to the strength of covalent bonding. Our results indicate that there is a remarkable dependence of the potential energy gradient of the proton between $A–H \cdots B$ and $A^- \cdots HB^+_{\text{(solvated)}}$ upon base structure.

Employing a variety of oxygen and nitrogen bases (similar to those for which critical differences were obtained in the work with *p*-FC_6H_4OH), the F nmr shifts of the 1:1 ion pair of the base with *p*-$FC_6H_4SO_3H$ have been measured at 0.02 *M* concentration in CH_2Cl_2 solution at 25°. The shift of *p*-$FC_6H_4SO_3^-$ under the same conditions has been obtained using the crown ether complex[4] of the Na^+ salt. The hydrogen-bonded ion pairs are shifted 1.2–3.8 ppm to lower field strength than this *p*-$FC_6H_5SO_3^-$ salt. This magnitude of shifts is essentially the same as that observed in the formation of 1:1 hydrogen-bonded complexes with *p*-FC_6H_4OH.[2] However, the scale of bases for the F nmr shifts for the hydrogen-bonded ion-pair system is markedly different than that for the hydrogen-bonded complex system (for example, the former tends to give amine > pyridine > carbonyl compound, whereas the latter gives the reverse order[2]). Table I lists typical results for both systems.

Table I. *p*-Fluorobenzenesulfonic Acid Hydrogen-Bonded Ion Pairs

		Ion-pair formation		*p*-FC_6H_4-$OH \cdots B$
Base	pK_A, H_2O	$-\Delta H°$, kcal	Δ,[a] ppm	Δ,[b] ppm
sym-Tetramethylguanidine	13.9	27.3	7.78	3.70
$(n\text{-Bu})_3N$	10.9	25.8	7.36	2.50
Et_3N	10.8	24.9	7.25	2.66
4-Dimethylaminopyridine	9.6	23.3	7.46	3.37
$C_6H_5CH_2NMe_2$	8.9	21.5	6.96	2.34
$(\text{Allyl})_3N$	8.3	21.4	6.94	2.10
4-Methylpyridine	6.0	16.6	6.92	2.70
$CF_3CH_2NEt_2$	(5.8)	16.1	6.62	(1.5)[d]
Pyridine	5.2	15.4	6.68	2.49
$C_6H_5NMe_2$	5.1	14.7	6.71	1.75
p-$BrC_6H_4NMe_2$	4.2	(13.7)	6.52	(1.6)[d]
3-Bromopyridine	2.8	11.7	6.18	1.99
m-$NO_2C_6H_4NMe_2$	2.6	(10.5)[c]	6.15	(1.1)[d]
Guaiazulene	1.4		(5.6)[e]	(1.2)[d]
p-$NO_2C_6H_4NMe_2$	0.6	(7.6)[c]	5.79	(0.7)
2,6-Dimethyl-γ-pyrone	0.4	5.5	5.83	2.98
Tetramethylurea	~0	6.4	5.68	3.00
N,*N*-Dimethylacetamide	−0.2	5.4	5.21	2.86

[a] Shifts relative to 0.02 *M* *p*-$FC_6H_4SO_3Et$ in CH_2Cl_2 at 25°, which may be taken as essentially equal to those for internal *p*-$FC_6H_4SO_3H$. Shift for crown ether Na^+ complex of *p*-$FC_6H_4SO_3^-$ in CH_2Cl_2 is 8.8 ppm; "apparent per cent proton transfer" obtained for each ion pair as 100Δ/8.8. [b] *Cf.* ref 2. [c] Value estimated from the relationship $-\Delta H° = 0.82[-\Delta H°_{TFA}] - 5.9$, where $\Delta H°_{TFA}$ is the heat of ion-pair formation with trifluoroacetic acid in CH_2Cl_2 solution. This relationship has been confirmed in unpublished results for the other bases of this table. [d] Value estimated from results for analog compounds; *cf.* ref 2. [e] Obtained at −40° with excess base; value uncertain.

The upfield F nmr shifts (given in Table I) for the formation of the *p*-$FC_6H_4SO_3^-$ ion pairs from *p*-FC_6H_4-SO_3H parallel quite closely the aqueous pK_A of the base (for bases with pK_A > 0, *cf.* Table I), whereas the shifts for formation of the *p*-FC_6H_4OH hydrogen-bonded complexes bear no simple correspondence to the pK_A values.[2] However, these latter shifts are well correlated[2] by pK_{HB} values, standard free-energy parameters

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(1) This work was supported in part by the Public Health Service. We also gratefully acknowledge the support of the National Science Foundation which made available the nmr spectrometer to the Chemistry Department.
(2) D. Gurka and R. W. Taft, *J. Amer. Chem. Soc.*, **91**, 4794 (1969), and references therein.
(3) (a) C. L. Beli and G. M. Barrow, *J. Chem. Phys.*, **31**, 300, 1158 (1959); (b) H. Baba, A. Matsuyama, and H. Kokubun, *Spectrochim. Acta, Part A*, **25**, 1709 (1969), and references therein.
(4) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).