butylphenol (VI) are observed.[6] Moreover, the radical concentrations decay only slowly with time and increase with increasing temperature in a reversible manner. On the reasonable assumption that the source of the radicals is the presence of and the reversible disassociation of dimers formed from these radicals, the experimental values of the heats of formation of the dimers were obtained from the plots of 2 log [ArO·]T/[ArO·]30° *vs.* 1/T (*cf.* Figure 1) and are summarized in Table I. These experimentally derived values are in quantitative agreement with the values calculated in the earlier work[2] for the heats of formation of the carbon–carbon nonenolized dimers II of the phenoxy radicals from V and VI.

(6) A similar observation is made for the 4-phenylphenoxy radical. However, the concentration of that radical decays to zero within a few minutes at 30°.

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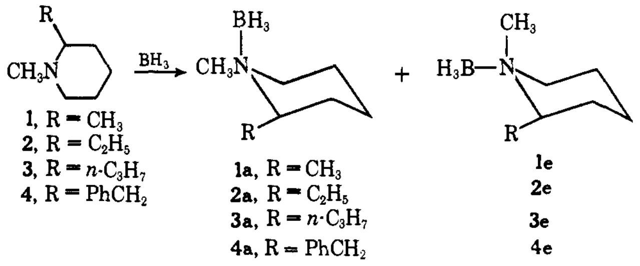
Stereochemistry of Amine–Boranes. I. Amine–Boranes from 1-Methyl-2-substituted Piperidines[1]

Sir:

The reaction of borane with conformationally biased piperidines has been shown to be similar in energetics to the quaternary salt formation with methyl halides or tosylates giving a preferential axial B–N bond formation.[1] Reaction of 1-methyl-4-*tert*-butylpiperidine with diborane in THF or with pyridine–borane gave a mixture of diastereomeric amine–boranes containing 85% of the isomer having an axial BH_3. This result is similar to that obtained for the quaternary salt formation with trideuteriomethyl tosylate.[2]

The stereoselectivity of quaternization of 1-methyl-2-substituted piperidines is less than that for the 3- or 4-substituted isomers,[3] and to test the similarity of amine–borane formation and quaternary salt preparation the reactions of borane in THF with 1,2-dimethylpiperidine (**1**), 1-methyl-2-ethylpiperidine (**2**), 1-methyl-2-*n*-propylpiperidine (**3**), and 1-methyl-2-benzylpiperidine (**4**) were investigated.[1] In each reaction a mixture of diastereomeric amine–boranes was formed and the composition could be determined from the integrated intensities of the NCH_3 signals of the amine–boranes in the pmr spectra of the mixtures. The assignment of pmr signals to the two diastereomeric structures was made on the basis of relative chemical shifts of the NCH_3 signals in the proton spectrum[4] and in the ^{13}C spectrum.[5] The results are given in Chart I. It can be seen that as the size of the 2 substituent increases, the relative amount of the diastereomer with the alkyl groups cis, formed by equatorial B–N bond formation, also increases.

Chart I



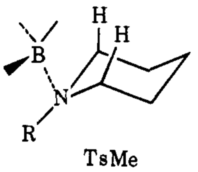
1, R = CH_3
2, R = C_2H_5
3, R = n-C_3H_7
4, R = $PhCH_2$

1a, R = CH_3
2a, R = C_2H_5
3a, R = n-C_3H_7
4a, R = $PhCH_2$

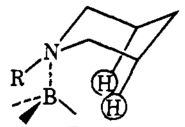
1e
2e
3e
4e

	Analysis of product mixture	Analysis after heating at 77°
1	84% **1a**; 16% **1e**	48% **1a**; 52% **1e**
2	79% **2a**; 21% **2e**	48% **2a**; 52% **2e**
3	71% **3a**; 29% **3e**	43% **3a**; 57% **3e**
4	68% **4a**; 32% **4e**	36% **4a**; 64% **4e**

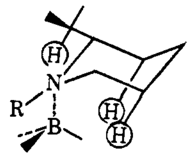
The factors affecting the relative stabilities of the diastereomeric transition states for the amine salt formation can be compared with those described for nucleophilic addition to cyclohexanones, for both reactions involve conversion of a tercovalent ring atom to a quadricovalent state. The data obtained in the amine–borane formation can readily be rationalized by considering the postulate proposed by Cherest and Felkin.[6] Thus, in the transition state of the formation of an equatorial B–N bond there would be the unfavorable torsional strain resulting from near eclipsing of the σ bonds of the axial 2 and 6 bonds with the developing B–N bond (transition-state model TSM-e). On the other hand, the developing B–N bond from the axial side introduces a steric, nonbonding interaction with the axial groups on the 3 and 5 positions (TSM-a).



TsMe



TsMa



TsMa′

The steric strain is smaller than the torsional strain in simple piperidines such as 1-methyl-3- or -4-substituted piperidines. Thus, axial B–N bond formation is favored as observed.[1] The introduction of a 2 substituent introduces a third nonbonded interaction (TSM-a′) which increases the energy of this transition state as the size of the 2 substitutent increases. This is reflected by a decrease in the stereoselectivity of the reaction.[7] These opposing effects in the transition states can be used to rationalize much of the quaternization data relating the effect of the structure of the

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(1) Portions of this research were discussed at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971, and at the IUPAC, Section Organo-Inorganic Chemistry, Boston, Mass., July 25–30, 1971. The research received financial support from research Grant No. PRF 3441-A1,4 from the American Chemical Society Petroleum Research Fund. The authors express their appreciation to the donors of this fund. All amine–boranes gave acceptable analyses for nitrogen and active hydrogen.

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

(3) Reviews on the stereochemistry of quaternary salt formation are: (a) J. McKenna, *Top. Stereochem*, **5**, 275 (1970); (b) A. T. Bottini in "Selective Organic Transformations," B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 89–142.

(4) The relative chemical shifts of the proton resonance in the nmr spectra of N,N-dialkylpiperidinium salts determined in $CDCl_3$ (A. T. Bottini and M. K. O'Rell, *Tetrahedron Lett.*, 429 (1967)) usually shows the resonance signal for the protons on the axial substituent at higher field than those on the equatorial group: ref 2 and G. Fodor, J. D. Medina, and N. Mandava, *Chem. Commun.*, 581 (1968).

(5) The authors express their appreciation to Professor Ernest Wenkert and David W. Cochran of Indiana University for determination of the ^{13}C magnetic resonance spectra. The discussion of these spectra will be published in a later paper.

(6) M. Cherest and H. Felkin, *Tetrahedron Lett.*, 2205 (1968).

(7) Reference 3b, pp 114–115.

alkylating agent and the structure of the nitrogen substituent with the isomer distribution in the product mixture.

On heating at 77° the amine–boranes underwent equilibration to give mixtures having the compositions shown in Chart I. In each case the axial conformation for the *N*-methyl is favored over NBH_3. The larger the size of the 2 substituent the greater is the amount of the isomer with the axial *N*-methyl.

Since the NBH_3 has been shown to have a slightly smaller effective size than the NCH_3 (the difference was estimated by equilibrium studies to be about 100 cal/mol),[1] this trend suggests that the nonbonded repulsion between two vicinal equatorial groups is greater than that between vicinal axial–equatorial substituents as was previously suggested.[8] These data do not allow for the calculation of the magnitude of this effect in absolute terms of $\Delta G_{ee} - \Delta G_{ae}$; however, it is interesting to note that the $\Delta\Delta G$ for the equilibria with R = CH_3 (**1a** ⇄ **1e**) and R = $PhCH_2$ (**4a** ⇄ **4e**) approximates the difference in conformational free energies for methyl (*ca.* 1.7 kcal/mol) and $PhCH_2$ (*ca.* 2.1 kcal/mol).[9]

(8) R. Lyle and J. J. Thomas, *Tetrahedron Lett.*, 897 (1969), and R. Lyle, J. Thomas, and D. Walsh in "Conformational Analysis," G. Chiurdaglu, Ed., Academic Press, New York, N. Y., 1970, pp 157–164.

(9) J. A. Hirsch, *Top. Stereochem.* 1, 199 (1967), and unpublished result of Dr. Edgar Garbisch, University of Minnesota.

(10) This work was abstracted from the thesis research of J. J. K. and E. W. S. to be presented to the Graduate School of the University of New Hampshire in partial fulfillment of the requirements of the Ph.D. degree.

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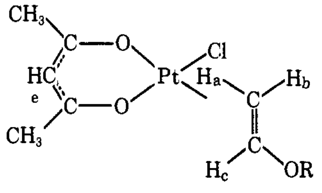
σ–π Rearrangements of Organotransition Metals. VII. A Platinum(II)–π-Vinyl Alcohol Complex. The General A_2X Appearance of the Vinyl Proton Nuclear Magnetic Resonances

Sir:

Two vinyl alcohol–transition metal complexes have been previously isolated. Ariyaratne and Green[1] have synthesized a vinyl alcohol π complex by protonation of dicarbonylcyclopentadienyl-(β-oxoethyl)iron. The nmr of this complex unexpectedly exhibited an A_2X pattern for the vinyl protons. Wakatsuki, Nozakura, and Murahashi[2] synthesized 1,3-bis(vinyl alcohol)-2,4-dichloro-μ-dichloro-platinum(II), although the nmr of this compound was not obtained due to its low solubility. Recently, Thyret reported that Wataksuki's work was not reproducible, and obtained evidence of the formation of (vinyl alcohol)iron tetracarbonyl at −80°.[3] We wish to report the preparation and characterization of a stable vinyl alcohol π complex of platinum(II) which also shows an A_2X pattern for the vinyl protons, due to a rapid equilibrium with a platinum–β-oxoethyl σ complex.

A viscous yellow oil, acetylacetonatochloro(π-vinyloxytrimethylsilane)platinum(II) (**1**), was prepared by treating acetylacetonatochloro(ethylene)platinum(II)[4] with vinyloxytrimethylsilane[5] in benzene. It was subsequently hydrolyzed by passing moist argon through a solution in *n*-hexane, precipitating a yellow powder of acetylacetonatochloro(π-vinyl alcohol)platinum(II) (**2**). This compound was purified by dissolution in dilute sodium hydroxide and reprecipitation as small crystals with HCl, 115–140° dec. It is not affected by air or water, but is rather thermally unstable, and should be stored in the refrigerator if it is to be kept longer than several days.

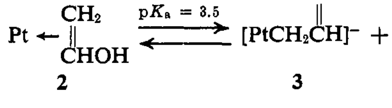
Anal. Calcd for $C_7H_{11}O_3PtCl$: C, 22.50; H, 2.97; Pt, 52.20; Cl, 9.49. Found: C, 23.37; H, 3.03; Pt, 52.16; Cl, 8.90. The ir spectrum (Nujol mull between CsI plates) of **2** showed (OH) at 3330 (s) and 3220 (s), $(C{=}C)_{\text{vinyl alcohol}}$ at 1551 (s), and (Pt–vinyl alcohol) at 411 cm^{-1} (m).



1, R = $Si(CH_3)_3$
2, R = H

The nmr of **1** showed the expected ABX pattern for the vinyl protons, whereas **2** in acetone exhibited an A_2X pattern (a 1 H triplet at δ 7.23, and a 2 H doublet at δ 3.90, *J* = 7.5 Hz). The acetylacetonato absorptions (Table I) were typical. In addition the vinyl ^{195}Pt–H coupling constants were very similar, as expected for a π complex: $J_{\text{Pt-H}_{ab}} = 76$ Hz, $J_{\text{Pt-H}_c} = 71$ Hz. If the acetone was very dry (less than four H_2O protons *ca.* δ 3.0), a broad 1 H resonance at δ 9.5 was visible, assigned to the OH proton.

The complex **2** could be titrated with sodium hydroxide in 50% aqueous acetone as a monobasic acid, $pK_a = 3.5$. Green made no quantitative measure of the acidity of the cyclopentadienyldicarbonyliron–π-vinyl alcohol cation, but from his description of its behavior it appears to be a still stronger acid, as might be expected from its positive charge. He was able to isolate both the π-vinyl alcohol and β-oxoethyl forms of the iron complex, while we have obtained **3** only as a yellow oil with large cations as tetra-*n*-butylammonium ion.



$$\mathrm{Pt} \leftarrow \underset{\mathrm{CHOH}}{\overset{\mathrm{CH_2}}{\|}} \;\underset{\longleftarrow}{\xrightarrow{pK_a\,=\,3.5}}\; [\mathrm{PtCH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H}]^- + \mathrm{H}^+$$

2 **3**

The spectra of **3** are similar to those of Green's iron complex, characteristic data being the ir absorption at 1650 cm^{-1} (C=O), and the nmr absorptions at δ 9.3 (1 H, t) and 3.3 (2 H, d), *J* = 5.5 Hz, again an A_2X pattern (see Table I). The Pt–H coupling constants also change from **2** to **3** in the expected manner. From the nearly equal values for $J_{\text{Pt-H}_{ab}}$ and $J_{\text{Pt-H}_c}$ of 71 and 76

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(1) J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 1 (1964).

(2) Y. Wakatsuki, S. Nozakura, and S. Murahashi, *Bull. Chem. Soc. Jap.*, 42, 273 (1969).

(3) H. Thyret, *Proc. Fifth Int. Conf. Organometal. Chem., 1971*, 2, 216 (1971).

(4) C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 1653 (1970).

(5) A. N. Nesmeyanov, I. F. Lutsenko, and V. A. Brattsev, *Dokl. Akad. Nauk. USSR*, 126, 551 (1959); F. Runge and W. Abel, *Makromol. Chem.*, 120, 148 (1968).