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** $\rightleftarrows$ **1e**) and R = $PhCH_2$ (**4a** $\rightleftarrows$ **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 Stereochem.* **1**, 199 (1967), and unpublished result of Dr.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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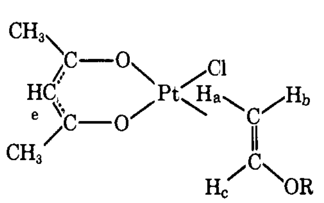
σ–π Rearrangements of Organotransition Metals. VII. A Platinum(II)–π-Vinyl Alcohol Complex. The General A_2X Appearance of the Vinyl Proton Nuclear Magnetic Resonances

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.

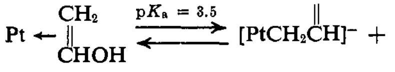
Anal. Calcd for $C_7H_{11}O_3PtCl$: C, 22.50; H, 2.97; Pt, 52.20; Cl, 9.49. Found: C, 23.37; H, 3.03; Pt, 52.16; Cl, 8.90. The ir spectrum (Nujol mull between CsI plates) of **2** showed (OH) at 3330 (s) and 3220 (s), $(C{=}C)_{\text{vinyl alcohol}}$ at 1551 (s), and (Pt–vinyl alcohol) at 411 cm^{-1} (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: $J_{Pt-H_{ab}}$ = 76 Hz, J_{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.



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

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 $J_{Pt-H_{ab}}$ and J_{Pt-H_c} of 71 and 76

(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).

Table I. Nmr Data[a] for **2**, **3**, and a 1:2 Mixture

(t)	**2**	**3**	**2–3** (1:2)	% shift
δH_c, ppm	7.27	9.16	8.48	64
$J_{H_{ab}-H_c}$, Hz	8	5.5	6.5	60
J_{Pt-H_c}, Hz	71	20	38	65
δH_{ab}, ppm	3.89	3.28	3.49	66
$J_{Pt-H_{ab}}$, Hz	76	113	99	64
δCH_3, ppm	1.99	1.68	1.80	61
δCH_3, ppm	1.89	1.64	1.73	64
δH_e, ppm	5.64	5.32	5.41	72

[a] At 100 MHz in aqueous acetone.

Hz in **2**, the two methylene protons of **3** show an increase to 114 Hz, and the aldehyde proton a decrease to 20 Hz.

Considering the acidity of the vinyl alcohol complexes, the equivalence of H_a and H_b is not surprising, since one would expect some ionization to take place in the polar solvents used, scrambling H_a and H_b. Evidence for this rapid equilibrium is seen in the nmr mixtures of **2** and **3**, which exhibit a single spectra with averaged J and δ values. Table I gives the data for solutions of pure **2**, **3**, and an approximately 1:2 mixture of the two, which shows values (column 4) consistently two-thirds of the way between **2** and **3**.

Although the ionization involves some atomic motion besides a proton transfer, the rate of ionization is rather high, since only a slight broadening of the vinyl proton absorptions of **2** is seen even in acetone 0.05 N in $HClO_4$, in which the ratio of **3** to **2** must be very small. At −20° in the absence of acid, the clean doublet–triplet pattern of an acetone solution of **2** changes to a rather nondescript multiplet, whose fine structure could not be resolved due to poor solubility. At the same time, the OH resonance sharpened into two singlets of nearly equal intensity at δ 9.84, 9.94, as the rate of proton exchange slowed. The two peaks could be due either to two isomers of **2**, resulting from the two possible orientations of the vinyl alcohol, or to coupling with one of the vinyl protons. Both of these changes presumably arise from the slowing of the exchange above.

Further investigations into this dissociation of other π-vinyl alcohol complexes are in progress, and will be reported later.

Acknowledgment. We wish to thank Professor S. Murahashi and Dr. Y. Wakatsuki for providing the detailed information on their experiments. We also gratefully acknowledge the financial support from the R. A. Welch Foundation.

(6) Arakawa Forest Chemical Industries, Ltd., Osaka, Japan.

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*Book Reviews**

Electron Microscopy and Plant Ultrastructure. By A. W. ROBARDS (University of York). McGraw-Hill, London. 1971. x + 298 pp.

The fine details of the structure of plant cells as revealed by electron microscopy are presented with abundant illustrations. There are leading references, a glossary, and a good index. Biochemists concerned with cellular biology should find this book useful.

Handbook of Molecular Constants of Inorganic Compounds. By K. S. KRASNOV, V. S. TIMOSHININ, T. G. DANILOVA, and S. V. KHANDOZHKO. Israel Program for Scientific Translations, 1970. Distributed in the U. S. A. by International Scholarly Book Services, Inc., Portland, Ore. v + 275 pp. $15.00.

Except for a 36-page chapter on methods of determination and calculation, this book consists entirely of tables and the associated notes and references. Values of internuclear distances, valency angles, vibration frequencies, dissociation energies, heats of formation, and electronic ground levels are given for 1400 gaseous inorganic compounds. The literature coverage is stated to be through 1966 and partly into 1967. Accessibility is aided by a formula index.

Technology of Inorganic Compounds (Chemical Engineers' Handbook). By D. D. MEL'NIK and E. B. MEL'NIKOV. Israel Program for Scientific Translations, 1970. Distributed in the U. S. A. by International Scholarly Book Services, Inc., Portland, Ore. iv + 248 pp. $13.00.

This book consists almost entirely of diagrams of various physical properties, such as solubility, heat capacity, vapor pressure, etc., as functions of temperature, pressure, or concentration. They are arranged in six "chapters": Nitrogen, Sulfur, Phosphorus, Halogens (and the inorganic compounds of each of these), Soda and Other Alkalis, and Salts and Some Other Inorganic Compounds. There is an appendix, a bibliography of 37 references (mostly to secondary sources), and an index.

Tables of Nuclear Quadrupole Resonance Frequencies. By I. P. BIRYUKOV, M. G. VORONKOV, and I. A. SAFIN. Israel Program for Scientific Translations, 1969. Distributed in the U. S. A. by International Scholarly Book Services, Inc., Portland, Ore. vi + 135 pp. $10.00.

This book is a translation of the Russian original published in 1968. It consists almost entirely of tables of nqr frequencies of compounds arranged in order of the position in the periodic table of the element being considered. Coverage is through 1966. It is a valuable compendium of information, but its usefulness is somewhat reduced by poor editorial practices. The tables are up to 47 pages long, but are printed with only the table number as a running heading, without a title; they are thus unnecessarily hard to follow. The references are given in an ambivalent alphabetical code (either Latin or Cyrillic alphabet), and since many of the letters are the same in each alphabet, one is left wondering, for example, whether reference C15 is to Cohen in *Physical Reviews* or to Semin, *et al.*, in *Zhurnal Fizicheskoi Khimii.* The summarizing of the Soviet contributions to this growing field is a helpful feature, even though it is not very recent.

Contemporary British Chemists. By W. A. CAMPBELL and N. N. GREENWOOD (University of Newcastle upon Tyne). Taylor and Francis Ltd., London. 1971. 286 pp. $16.00.

In a world of harsh necessities and urgent deadlines, it is always a pleasure to stop the clock—and even turn it back a little—and indulge in some of the more leisurely pursuits of earlier times.

This book brings with it themes both ancient and modern-ancient, in that space is used with an almost total disregard to costs, the paper is excellent, and, for the most part, the photographs are

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* Unsigned book reviews are by the Book Reviews Editor.