A shift *vs.* concentration analysis[7] was used to obtain an ion association constant, $K$, and limiting shift, $\Delta$, where $K = (1 - \gamma)/C\gamma^2$, $C$ is the stoichiometric salt concentration, and $\Delta = \nu_{\text{paired}} - \nu_{\text{free}}$. Concentration ranges studied were generally from about 0.004 to 0.1 $M$. Samples were run on a Varian A-60-A spectrometer and chemical shifts relative to internal TMS ($\sim$1% v/v) were determined by standard side-band techniques. A computer of average transients was used when needed.

Although in the solvents studied the salt concentrations exceed the limits of applicability of Debye–Hückel theory,[8] we attempted to introduce extended Debye–Hückel activity coefficients to the analysis. This yielded extremely large values for $\Delta$ (greater than 400 Hz) which are physically unreasonable, and subsequently the data were analyzed without applying corrections due to ionic atmosphere effects. A simple ion-pair mechansim[7] describes the data well, no experimental point being more than 0.25 Hz from its calculated value.

**Table I.** Association of Methyltributylammonium Tetraphenylboride in Various Nonaqueous Solvents

| Solvent | Dielectric constant[a,b] | $K_{\text{nmr}}$, l./mole[a] | $-\Delta$, limiting shift, Hz | $K_{\text{conductivity}}$ l./mole[c] |
|---|---|---|---|---|
| Acetonitrile | 34.3 | 1.25 ± 0.3 | 75 ± 10 | 6.0,[d] 2.2,[e] 0.0[f] |
| Nitromethane | 34.2 | 1.55 ± 0.3 | 80 ± 10 | 0.0[f] |
| Nitrobenzene | 32.2 | 4.9 ± 0.9 | 79 ± 10 | 4.7[g] |
| Benzonitrile | 24.0 | 20.0 ± 3.0 | 33 ± 2 | |
| Acetone | 19.3 | 25.0 ± 3.0 | 32 ± 1 | 91.0[e] |

[a] At 40 ± 2°. [b] Estimated using data provided in A. A. Maryott and E. A. Smith, "Table of Dielectric Constants of Pure Liquids," NBS Circular No. 514, U. S. Government Printing Office, Washington, D. C., issued Aug 1951. [c] At 25°. [d] Reference 2b. [e] J. F. Coetzee and D. K. McGuire, *J. Phys. Chem.*, **67**, 1810 (1963). [f] J. F. Coetzee and G. P. Cunningham, *J. Amer. Chem. Soc.*, **87**, 2529 (1965). [g] Reference 2a.

Table I displays the results for five solvents and conductivity results for the analogous tetrabutylammonium salt, when available. The association constant increases and the limiting shift decreases as the dielectric is lowered. The trend for the nmr association constant is qualitatively in agreement with simple theory,[4] although there is marked curvature in a log $K$ *vs.* $1/D$ plot. The trend in the limiting shift provides new information. $\nu_{\text{free}}$ and $\nu_{\text{paired}}$ depend explicitly on the magnetic environment of the solvent. We assume $\Delta$ is only a function of the average distance between the $\alpha$-methyl group of the cation and the phenyl rings[5] of the anion in an ion pair for a given solvent because of the large magnetic anisotropy of the phenyl rings of the anion. Note that $\Delta$ is approximately the same in the three nearly isodielectric solvents, nitromethane, acetonitrile, and nitrobenzene. This fact and the magnitude of the shift suggest that a considerable fraction of the ion pairs are of the contact variety in the above-mentioned solvents. The much smaller limiting shifts in benzonitrile and acetone indicate that the ion pair on the average is not as "tight" as it is in the higher dielectric solvents. It must be emphasized that continuum theory[4] predicts that the interionic distance will be independent of both solvent and dielectric constant. Our findings are consistent with recent conductivity experiments which have revealed the general tendency of the contact distance in an ion pair to increase at lower dielectric constant, an effect possibly attributable to solute–solvent interaction.[3] Other effects possibly due to specific solvation are the increase of the effective Stokes radius of ions at lower dielectric constant[9] and the nonlinearity of plots of log $K$ *vs.* $1/D$.[10] We believe our results represent independent experimental observation of specific solute–solvent interactions.[11]

The temperature dependence of the chemical shifts is of extreme interest. Present theories[4] of ion association predict less association at lower temperatures and it is generally assumed[4b] that the interionic distance will be temperature independent as well. Thus one expects the $\alpha$-methyl resonance to be shifted *downfield* at lower temperature. In all our studies the $\alpha$-methyl resonance appeared further *upfield* at lower temperature (relative to the value of $\nu_{\text{free}}$ at that temperature), indicating either greater association or the formation of "tighter" ion pairs.[12]

Inasmuch as the alkylammonium tetraphenylborides have served as model salts in the investigation of the "sphere in continuum" model[14] of ion association, we believe the observed trend in limiting shifts and the temperature dependence effects provide further evidence questioning the validity of this model of association. The nmr method provides an independent means for obtaining both association constants *and* information pertaining to interionic separations. The usefulness of this technique and the questions raised here concerning the current theories[4] of ion association have prompted us to undertake a more complete study of the problem.

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(7) For methods of calculation see, for example (a) I. D. Kuntz and M. D. Johnston, *J. Amer. Chem. Soc.*, **89**, 6008 (1967); (b) R. L. Buckson and S. G. Smith, *J. Phys. Chem.*, **68**, 1875 (1964).

(8) Reference 6, p 106.

(9) D. F. Evans and P. Gardam, *J. Phys. Chem.*, 73, 158 (1969).

(10) H. K. Bodenseh and J. B. Ramsey, *ibid.*, **67**, 140 (1963).

(11) Alternatively, Bjerrum's model [N. Bjerrum, *Kgl. Danske Videnskab. Selskab*, 7, No. 9 (1926)] which predicts formation of more distant ion pairs at lower dielectric may be more applicable than the currently accepted Fuoss–Denison–Ramsey[4] model which allows for the formation of contact ion pairs only: G. Atkinson and S. Petrucci, *J. Phys. Chem.*, 70, 3122 (1966).

(12) It is interesting to note that Larsen[13] observed the same temperature dependence in his nmr studies of the association of the tetramethylammonium ion with the hexacyanoferrate(III) ion in water.

(13) D. W. Larsen and A. C. Wahl, *Inorg. Chem.*, **4**, 1281 (1965).

(14) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1871 (1963).

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## Hydroplatination of an Acyclic Diolefin

*Sir:*

The reaction of diene–platinum(II) halide complexes with alkoxides,[1] amines,[2] and carbanions[3] proceeds by nucleophilic attack on one of the diene double bonds to afford $\sigma$-bonded organoplatinum complexes (**1**, Y = nucleophile). We wish to report an unusual reaction

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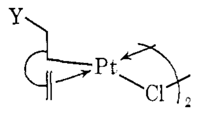
(1) J. K. Stille and R. A. Morgan, *J. Am. Chem. Soc.*, **88**, 5135 (1966), and references therein.

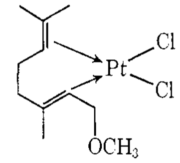
(2) G. Paiaro, A. DeRenzi, and R. Palumbo, *Chem. Commun.*, 1150 (1967).

(3) H. Takahashi and J. Tsuji, *J. Am. Chem. Soc.*, 90, 2387 (1968).

that yields what is apparently the first example of an analogous σ-bonded complex (**1**, Y = H), formally derived by the addition of hydride to one of the diene double bonds.



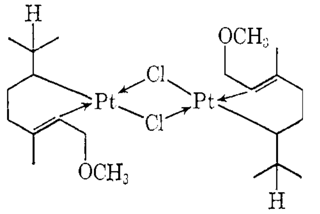
**1**



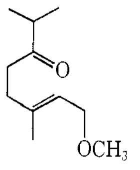
**2**

The platinum chloride complex **2** of geranyl methyl ether was required during the course of other work. Although no previous preparations of π complexes of such highly substituted acyclic diolefins could be found, the conditions used to prepare the analogous platinum complex of 1,5-hexadiene[4] were investigated. Geranyl methyl ether (excess) was stirred with potassium tetrachloroplatinite in aqueous ethanol at room temperature for 2–4 days; the mixture became acidic as the reaction progressed. The resulting precipitate was isolated and recrystallized from ether to afford a white crystalline solid, mp 147–150° (decomposition after melting), in 36% yield.

This product could be assigned the dimeric σ-bonded structure **3** on the basis of its elemental analysis, osmometric molecular weight, mass spectrum, and nmr spectrum. The latter (60 MHz, $CCl_4$) exhibited a pair of doublets (6 H, $J = 7$ Hz) at $\delta$ 0.88 and 1.15 assigned to the nonequivalent methyls of the isopropyl group, and singlets at 1.79 (3 H) and 3.33 (3 H) assigned to the vinyl and ether methyl groups, respectively. The resonance at 1.79 was flanked by satellites ($J = 56$ Hz) due to coupling to $^{195}Pt$ (abundance 34%). The other protons appeared in the spectrum as complex multiplets. One of these multiplets, $\delta$ 3.4–4.2 (3 H), could be assigned to the ABC pattern expected of the vinyl and methoxymethylene protons. The mass spectrum of **3** exhibited isotopic clusters at $m/e$ 796–804 ($M^+$) and 398–402 [$(M/2)^+$]; the relative abundances of the ions in each cluster were in excellent agreement with those required by natural isotopic abundances. Hydrogenation of **3** in ethanol yielded tetrahydrogeranyl methyl ether, indicating that no skeletal rearrangement had occurred.



**3**

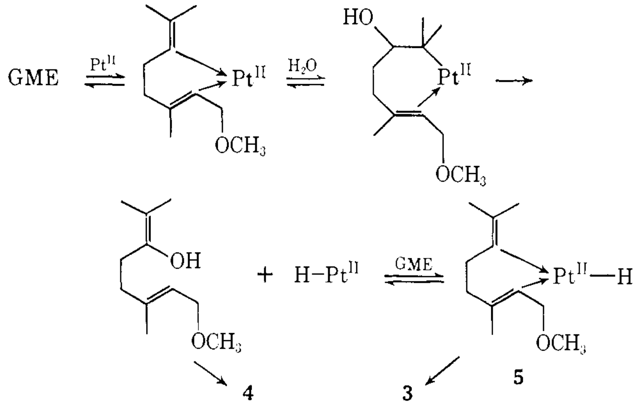


**4**

The unsaturated ketone **4** and several other as yet unidentified platinum complexes (none of which appear to be the π complex **2**) were also obtained from the reaction mixture. The ketone, isolated in 39% yield,[5] was assigned structure **4** on the basis of spectral data and an independent synthesis from geranyl methyl ether.

The σ-bonded complex **3** and the ketone **4** were also obtained, but in lower yield, by treatment of geranyl methyl ether with $[PtCl_2(C_2H_4)]_2$ (Zeise's dimer)[6] in acetone, followed by addition of water. In order to determine the source of the hydride needed for formation of **3**, the reaction with Zeise's dimer was carried out in deuterioacetone–$D_2O$, and reactions with potassium tetrachloroplatinite were conducted in EtOD–$D_2O$ and *t*-BuOD–$D_2O$. In all cases, the nmr spectrum of the resulting complex **3** exhibited some singlet isopropyl methyl resonance superimposed on each of the previously observed doublets. From the relative intensities of these lines it was estimated that in each case the complex only contained about 30% deuterium at the isopropyl carbon, thus indicating the primary source of hydride to be the geranyl methyl ether (GME) itself. These results are consistent with reaction Scheme I.

**Scheme I**



The incorporation of deuterium into **3** would occur by partial exchange of the complexed platinum hydride (**5**) with solvent protons[7] prior to its collapse to **3**. Similar mechanisms involving reversible addition of platinum hydrides to olefins have been proposed for the platinum-catalyzed isomerization of olefins.[8] Chatt and coworkers[9] have prepared platinum alkyls by the addition of *trans*-$[PtHCl(PEt_3)_2]$ to 1-olefins, but the reaction failed when applied to internal olefins. Interestingly enough in this respect, we find that treatment of **3** with triphenylphosphine in tetrahydrofuran results in rapid reaction to produce geranyl methyl ether and *trans*-$[PtHCl(PPh_3)_2]$.

Investigations aimed at determining the structures of the other complexes formed in the above reactions, as well as trapping the intermediate π complex **2** are currently underway.

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[4] K. A. Jensen, *Acta Chem. Scand.*, 7, 866 (1953).

[5] When the reaction was allowed to proceed for 15 days, the complex **3** and ketone **4** were isolated in yields of 71 and 68%, respectively.

[6] J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 210 (1957).

[7] C. D. Falk and J. Halpern, *J. Am. Chem. Soc.*, **87**, 3523 (1965).

[8] J. F. Harrod and A. J. Chalk, *ibid.*, **86**, 1776 (1964); R. Cramer and R. V. Lindsey, Jr., *ibid.*, **88**, 3534 (1966); H. A. Tayim and J. C. Bailar, Jr., *ibid.*, **89**, 3420 (1967).

[9] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc., A*, 190 (1968).