This is substantiated by data (examples in Table I) on metastable peaks formed in 72 processes producing major fragment ions in a variety of spectra. For the 25 in which $[m^*]/[d] < 0.01\%$, all but 3 involve simple bond cleavages. For one of these a nonrearrangement path is possible; for the others the rearranged product ions exhibit abundances $<5\%$. Values of $[m^*]/[d] > 0.01\%$ are shown by 34 processes apparently involving rearrangement. Large values can also arise from particular cleavages, such as $M - CH_3$, and those involving secondary decompositions. Some types of reactions for particular compound classes show self-consistent $[m^*]/[d]$ values. It appears that with certain modifications, such as a correction for competing reactions, this value may provide a quantitive characteristic of reaction type.

**Acknowledgment.** The authors are indebted to M. L. Gross, B. S. Rabinovitch, D. J. McAdoo, and R. E. Davis for helpful discussions and to the National Institutes of Health for financial support.

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## The Nature of the So-Called Coordination Compound $(Azobenzene)_2PtCl_4$

*Sir:*

The compound $(AB)_2PtCl_4$ (AB = azobenzene) reported by Kharasch and Ashford[1] has often been cited as an example of the coordinating ability of the azo group,[2-4] and olefinic type bonding has been suggested.[1,5] Since we have observed that the bonding of *cis*-aliphatic azo compounds to platinum(II)[6] occurs through the lone pairs on the nitrogen atoms, it was of interest to us to further characterize this compound.

Following Kharasch and Ashford's procedure, 1 g of *trans*-azobenzene was added to 0.5 g of $PtCl_4$ in 10 ml of glacial acetic acid, and the mixture was warmed on the steam bath for 1 hr. A brick red solid is precipitated after the platinic chloride dissolves. (If hydrated platinic chloride is used, the same compound precipitates almost immediately.) The precipitate appears soluble in organic solvents as reported by Kharasch and Ashford, and as such supports their formulation. However, if the solvents are dried over a molecular sieve, the solid is totally insoluble. Elemental analysis revealed that the compound has the empirical formula $[AB\text{-}H^+]_2PtCl_6{}^{2-}$. Elemental analysis of the solid after washing with wet solvents gives values for C and N which decrease as washing progresses, although their ratio remains constant. Simultaneously the percentage of platinum increases from 25.0 to 30.7% depending on the amount of washing. This indicates that trace amounts of water partially hydrolyze the conjugate acid to free azobenzene which colors the wash liquid. There is no true solubility of the compound. Since the earlier workers analyzed only for platinum, the platinum content appropriate to their suggested complex $(AB)_2PtCl_4$, 27.84%, can be reached in the course of washing.

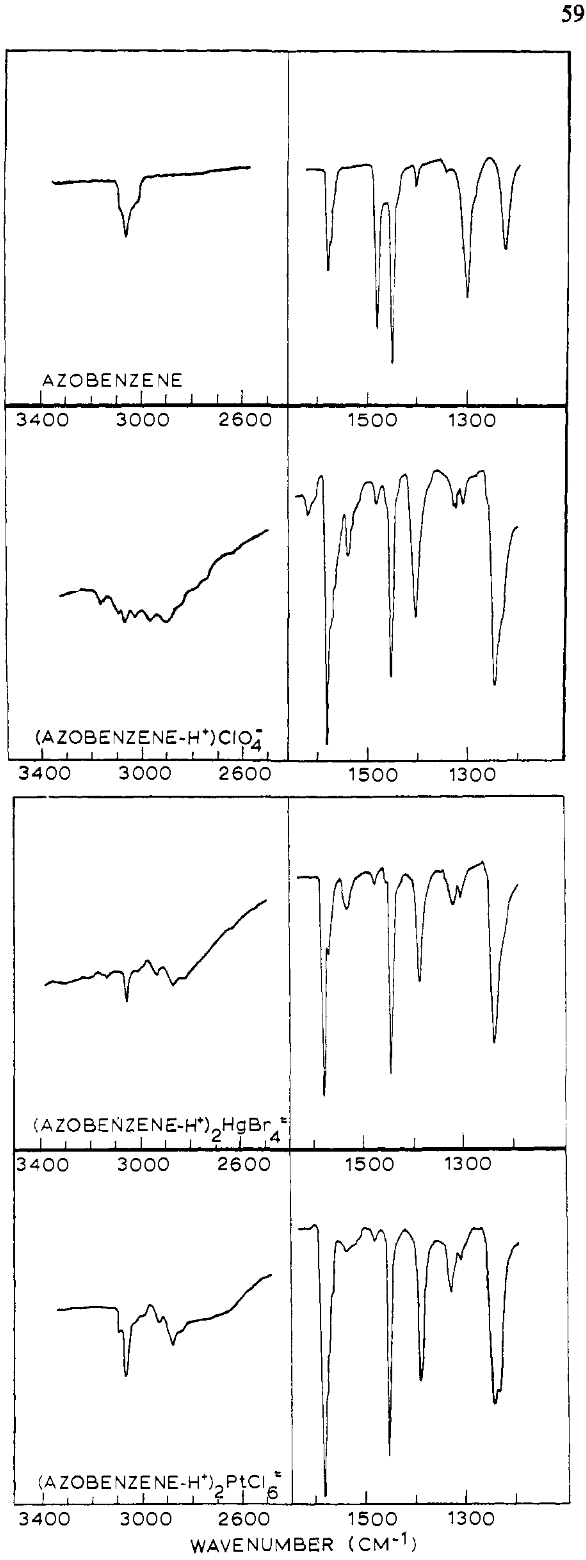

Figure 1. Infrared spectra.

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**Table I.** Analytical Results

| | | % C | % H | % N | % Cl | % Pt |
|---|---|---|---|---|---|---|
| $H^+$ | Calcd | 37.10 | 2.84 | 7.23 | 27.50 | 25.00 |
| $[C_6H_5N{=}NC_6H_5]_2PtCl_6^{2-}$ | Found | 36.47 | 2.89 | 7.26 | 28.38 | 25.20 |
| $H^+$ | Calcd | 32.50 | 2.50 | 6.30 | | |
| $[C_6H_5N{=}NC_6H_5]_2HgBr_4^{2-}$ | Found | 32.05 | 2.60 | 6.11 | | |
| | | 31.70 | 2.52 | . . . | | |
| $H^+$ | Calcd | 50.90 | 3.89 | 9.90 | | |
| $[C_6H_5N{=}NC_6H_5]ClO_4^-$ | Found | 50.71 | 3.97 | 10.14 | | |

Further evidence that the compound was a salt was obtained from a comparison of its ir spectrum with the spectra of other azobenzene salts. $[AB\text{-}H^+]ClO_4^-$ was prepared by the method of Jaffé.[7] (We find that this compound is not hygroscopic, although it has been described as such.[7]) The perchlorate can also be prepared by mixing together acetic acid solutions of 70% $HClO_4$ and azobenzene. Acetic acid appears to be a good solvent for preparing the conjugate acid salts of azobenzene. $[AB\text{-}H^+]_2HgBr_4^{2-}$ was prepared by bubbling anhydrous HBr through a mixture of 0.5 g of $HgBr_2$ and 10 ml of glacial acetic acid until all the $HgBr_2$ had dissolved followed by the addition of 1.0 g of azobenzene in 20 ml of glacial acetic acid. The precipitate which formed immediately was filtered and washed repeatedly with glacial acetic acid and then with dry hexane. Analytical results are collected in Table I.

The infrared spectra of all the azobenzene conjugate acid salts are very similar but are different from the spectrum of azobenzene. Figure 1 shows the region above 2500 cm$^{-1}$, containing the N–H stretch and aromatic C–H stretch vibrations, and the region 1200–1600 cm$^{-1}$. These were obtained in dry hexachlorobutadiene and Nujol mulls. The ir band at 1390 cm$^{-1}$ in the salts is absent in free azobenzene and is assigned to the N=N stretch. The presence of this band is expected from the asymmetry introduced by protonation. The Raman spectrum of solid azobenzene shows a strong polarized band at 1440 cm$^{-1}$, but in $[AB\text{-}H^+]\cdot ClO_4$ this band is absent and a strong new band is found at 1407 cm$^{-1}$. Large relative intensity changes also occur in three of the typical aromatic ring breathing modes at 1580, 1480, and 1450 cm$^{-1}$. The strong band at 690 cm$^{-1}$ in azobenzene is shifted to 670–675 cm$^{-1}$ in the salts and is a useful indicator for the presence of free azobenzene resulting from partial hydrolysis.

In contrast to our results, Jaffé observed that the ir spectrum in KBr disks of azobenzene and its perchlorate salt were very similar. We find that the spectra of all the salts in KBr disks show the presence of free azobenzene, which may be liberated either by hydrolysis due to traces of water always present in KBr disks, or by interaction with $Br^-$. These possibilities are suggested by our observations that (a) wet organic solvents cause hydrolysis and (b) the compound $[AB\text{-}H^+]Br^-$ is unstable with respect to azobenzene and HBr in dry air at room temperature.

The yield of $[AB\text{-}H^+]_2PtCl_6^{2-}$ shows that 50% of the platinum is consumed by formation of the salt. Since $PtCl_4$ is the only source of chloride ion, the yield cannot exceed 66%. If the filtrate from the reaction is evaporated to dryness and the residue washed repeatedly with dry hexane, a dark brown solid is obtained which contains platinum, azobenzene, and acetate. This compound has not been fully characterized.

We conclude that the compound formulated by Kharasch and Ashford as $[azobenzene]_2PtCl_4$ is in fact $[azobenzene\text{-}H^+]_2PtCl_6^{2-}$, a salt with no coordination of the azobenzene to platinum. The infrared spectrum of azobenzene is quite different from that of its conjugate acid, and the similarity reported by Jaffé was probably due to decomposition in the KBr disks.

The coordination compounds of azobenzene include an $SbCl_5$ adduct[8] and some uncharacterized silver and copper complexes.[4] The present work indicates that there is, as yet, no evidence for $\pi$-olefinic type bonding of azobenzene.

**Acknowledgment.** We thank the National Science Foundation Grant (GP-6850) for support of this research.

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## Flash Photolysis of 5-Diazo-10,11-dihydrodibenzo[*a*,*d*]cycloheptenylidene

*Sir:*

Recent studies on the optical spectroscopy[1–4] and electron spin resonance (esr)[5–8] of a number of aromatic methylene intermediates have revealed the molecular structure of carbenes to a considerable extent. It is doubtful, however, that one is entitled to discuss the reactivity of carbenes produced at room temperature in connection with the information obtained at 77°K by optical spectroscopy and esr studies. Furthermore, although there have been reported several electronic spectra of methylene[9] and halomethylenes[10] by the flash

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