

Although a number of cyclic and acyclic π -pentadienyliron tricarbonyl salts are known,⁴ the present structure is unique in that the five-carbon unit comprising the cationic skeleton is not contained within a continuous carbon chain.⁹ As would be required for a symmetrically bound allyl group, the C-2-C-3 and C-3-C-4 bond lengths are equal within the present level of accuracy. These, with the C-6-C-7 bond, are as expected intermediate between a single and a double bond. While the angles defined by C-1, C-2, C-3, C-2, C-3, C-4, and C-3, C-4, C-5 are close to the values expected for trigonally hybridized carbon atoms, it is significant that carbon atoms C-1 and C-5 are not coplanar with the allyl group but lie instead 0.52 Å. above the plane defined by C-2, C-3, and C-4.¹⁰ The displacement of bonds to the termini of the allyl group from trigonal toward tetrahedral geometry is comparable with, although smaller in degree than, the analogous distortions observed in several cyclic dieneiron tricarbonyl complexes.¹¹ It has been suggested^{11d} that these distortions are to be accounted for in terms of σ -bonding of the terminal carbon atoms of the butadiene group to the metal atom, but it is clear that such a description is less satisfactory in the present context, unless three-point attachment of the allyl group to a seven-coordinated metal atom be considered.^{11a} In any event, distortions in the σ -framework of the ligands which result in increased overlap of metal and carbon 2p-orbitals, as well as those imposed by the geometry of the ligand and induced by back bonding from the metal atom to antibonding levels in the ligand, cannot be neglected.

The structure of the complex cation does not appear to be significantly different in solution. Its n.m.r. spectrum displays signals at τ 5.05 (triplet, $J = 6$ c.p.s.), 5.32 (triplet, $J = 6$ c.p.s.), 5.76 (pair doublets, $J \approx J' = 2$ c.p.s.), and 6.62 (multiplet), assignable to H_3 , $H_{2,4}$, $H_{6,7}$, and $H_{1,5}$, respectively, and consistent with a structure for the cation essentially identical with that found in the crystalline state. Moreover, the couplings of $H_{8\alpha}$ (τ 8.86) and $H_{8\beta}$ (τ 8.30) (1) with the bridgehead protons ($H_{1,5}$) are unequal ($J_{\alpha,1} = 1$ c.p.s., $J_{\beta,1} = 4$ c.p.s., $J_{\alpha,\beta} = 12$ c.p.s.), in accord with the molecular geometry defined in Figure 1.¹²

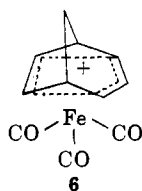
Acknowledgment. We thank the Computation Center

(9) Several π -allyliron tricarbonyl salts have recently been described by G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962), and G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind. (London)*, 836 (1964).

(10) The dihedral angle between the least-squares plane fitted to C-1, C-2, C-4, and C-5 and the plane defined by C-2, C-3, and C-4 is 161°.

(11) (a) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962); (b) M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 226 (1964), (c) R. P. Dodge, *J. Am. Chem. Soc.*, **86**, 5429 (1964); (d) D. L. Smith and L. F. Dahl, *ibid.*, **84**, 1743 (1962).

(12) The pronounced deshielding of $H_{6,7}$ protons in the cation, as is evident from a comparison of the chemical shift of these protons with those in the neutral complex (τ ca. 6.7), suggests that contributions from more highly delocalized charged forms such as 6 may be important, although transmission of electronic effects through the ligand-metal orbitals cannot be discounted.



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Selective Catalysis of the Copolymer of 4(5)-Vinylimidazole and Acrylic Acid

Sir:

The efficiency of multicenter enzymatic catalysis is sometimes partially due to the electrostatic attraction that one of these functions exerts on a charged substrate. This could be the case with ribonuclease¹ and acetylcholinesterase.² For acetylcholinesterase a negatively charged site A besides a catalytic function B was recognized in the active site. The role of A was considered to be electrostatic attraction of the positively charged substrate, acetylcholine, which improved the catalytic action of group B from a "neighboring group position." While group A could be the carboxylate anion, group B (or part of it) was identified as imidazole.³

As a macromolecular model for acetylcholinesterase the copolymer of 4(5)-vinylimidazole and acrylic acid has been prepared. Partially protonated homopolymers of 4-vinylpyridine,^{4,5} 4(5)-vinylimidazole,⁶ and N-vinylimidazole⁷ were found effective with negatively charged substrates. Bell-shaped pH-rate profiles were realized⁵⁻⁷ since partial ionization optimized the cooperative effect of polymer charge and nucleophile concentration. Separation of the roles of electrostatic attraction and catalytic action between two different functional groups A and B in a copolymer makes it possible to vary independently the charge of the polymer and the concentration of catalytically active groups. The assistance of the charged groups to the catalytic functions must be through coiling of the polymer chain.⁸ A proper concentration of charged groups in the copolymer may produce optimal results.⁹ So far, the possibility to improve the catalytic action of a group B by its random copolymerization with a noncatalytic charged group A has not been validated. We wish to report the first example of a synthetic copolymer with a marked selective catalysis.

In benzene solution 0.0056 mole of 4(5)-vinylimidazole and 0.0053 mole of acrylic acid were polymerized at 70° for 12 hr. with azobisisobutyronitrile as an initiator. The copolymer was obtained in 55% con-

(1) C. H. W. Hirs, M. Halmann, and J. H. Kycia in "Biological Structure and Function," Vol. I, Academic Press Inc., New York, N. Y., 1962, p. 41.

(2) I. B. Wilson in "Enzymes," Vol. IV, P. D. Boyer, H. A. Lardy, and K. Myrback, Ed., Academic Press Inc., New York, N. Y., 1960, pp. 501-520.

(3) I. B. Wilson and F. Bergmann, *J. Biol. Chem.*, **185**, 479 (1950); I. B. Wilson, *ibid.*, **197**, 215 (1952); F. Bergmann, I. B. Wilson, and D. Nachmansohn, *ibid.*, **186**, 693 (1950).

(4) H. Ladenheim, E. M. Loebel, and H. Morawetz, *J. Am. Chem. Soc.*, **81**, 20 (1959).

(5) R. L. Letsinger and T. J. Savereide, *ibid.*, **84**, 114, 3122 (1962).

(6) C. G. Overberger, T. St. Pierre, N. Vorchheimer, and S. Yaroslavsky, *ibid.*, **85**, 3513 (1963); C. G. Overberger, T. St. Pierre, N. Vorchheimer, J. Lee, and S. Yaroslavsky, *ibid.*, **87**, 296 (1965).

(7) R. L. Letsinger and I. Klaus, *ibid.*, **86**, 3884 (1964).

(8) Cf. P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, New York, N. Y., 1953, p. 95.

(9) The effect of copolymer composition on catalytic action is now being investigated.

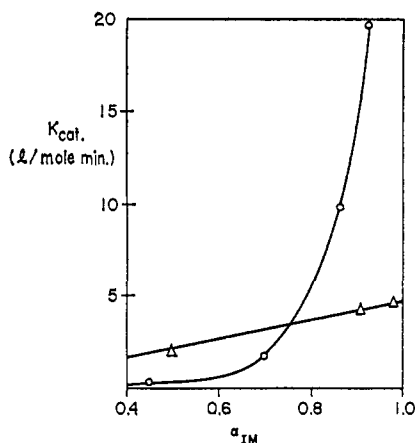
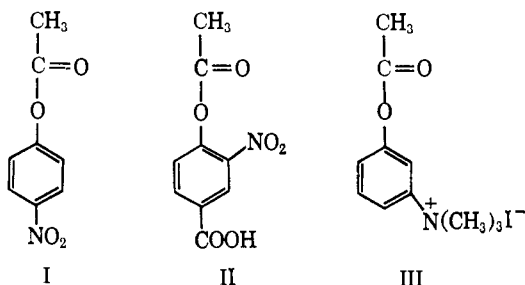


Figure 1. Solvolysis of 3-acetoxy-N-trimethylanilinium iodide by imidazole (Δ) and by the copolymer of 4(5)-vinylimidazole and acrylic acid (O).

version and contained the two monomers in 0.77:1.00 molar ratio, respectively. The esterolytic action of this catalyst was tested with a neutral, negatively, and positively charged substrate, *i.e.*, *p*-nitrophenyl acetate (I), 4-acetoxy-3-nitrobenzoic acid (II), and 3-acetoxy-N-trimethylanilinium iodide (III).



Rates were measured at 26° in 28.5% EtOH with Tris buffers and ionic strength 0.02. The reactions were followed spectrophotometrically at the absorption maximum of the corresponding phenols: for I, at 400 $m\mu$; for II, at 416 $m\mu$; and for III, at 277 (pH 7 and 8) and 293 $m\mu$ (pH 9). The results were compared with solvolysis catalyzed by monomeric imidazole. With the copolymer and monomer all substrates followed pseudo-first-order kinetics.

The copolymer showed marked selectivity toward the positively charged substrate. Only with this substrate the rate of copolymer catalysis was better than that of the monomer (at high pH values).

Spectrophotometric and potentiometric titrations afforded the relation between pH and the degree of dissociation of imidazolium residues¹⁰

$$\text{pH} = 7.2 - 2.1 \log \frac{1 - \alpha_{\text{IM}}}{\alpha_{\text{IM}}}$$

Near the isoelectric point (*ca.* 5.4) the copolymer was insoluble in the solvents employed. The catalytic rate constants for the hydrolysis of the positively charged substrate, III, appear in Table I and are plotted *vs.* α_{IM} in Figure 1. Above pH 8.0 the copolymer is a better catalyst than imidazole, the catalytic power at pH 9.5 being higher by a factor of four. The enhanced catalytic efficiency of the copolymer can be

(10) Cf. A. Katchalsky and P. Spitnik, *J. Polymer Sci.*, **2**, 432 (1957); A. Katchalsky, N. Shavit, and H. Eisenberg, *ibid.*, **13**, 69 (1954); I. Kagawa and H. P. Gregor, *ibid.*, **23**, 477 (1957).

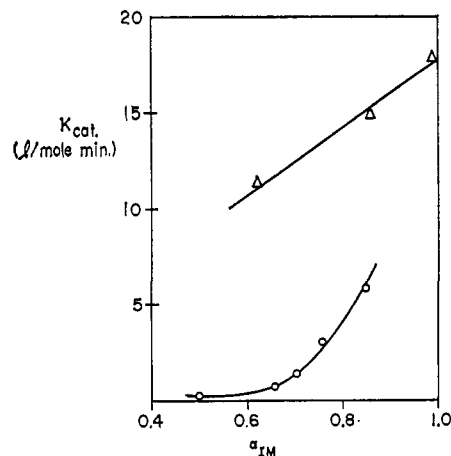


Figure 2. Solvolysis of *p*-nitrophenyl acetate catalyzed by imidazole (Δ) and by the copolymer of 4(5)-vinylimidazole and acrylic acid (O).

explained as the result of electrostatic attraction of the cationic substrate to the negatively charged sites of the copolymer, in this way improving the catalytic action of the imidazole groups.

With the negatively charged substrate, II, rates were strongly depressed relative to imidazole catalysis (Table II). The strong electrostatic repulsion between the copolymer and substrate carboxylate anions almost prevents interaction.

Table I. Catalytic Rate Constants^a of Imidazole and the Copolymer of 4(5)-Vinylimidazole and Acrylic Acid with 3-Acetoxy-N-trimethylanilinium Iodide

pH	Copolymer	Imidazole
7.0	0.3	1.9
8.0	1.8	4.3
8.8	9.9	4.5
9.5	19.4	4.7

^a Liters mole⁻¹ min.⁻¹.

Table II. Catalytic Rate Constants^a of Imidazole and the Copolymer of 4(5)-Vinylimidazole and Acrylic Acid with 4-Acetoxy-3-nitrobenzoic Acid

pH	Copolymer	pH	Imidazole
6.8	1.1	7.2	24.4
7.8	1.0	8.2	31.9
8.6	0.9	9.0	34.5

^a Liters mole⁻¹ min.⁻¹.

With the neutral substrate, I, the copolymer shows about 30% of the monomer activity at pH 8.8, while at pH 7.2 its rate is only 3% of the monomer rate. In Figure 2 the rates of monomer and copolymer catalysis are plotted *vs.* α_{IM} . In contrast to the monomer the catalysis by the copolymer is not proportional to α_{IM} . Analogous behavior was previously noticed for poly(4-vinylpyridine).⁵ This may be partly due to a variation in the degree of solvation of the substrate in the polyion as the state of ionization of the polymer is being varied with pH.¹¹

Acknowledgment. The authors gratefully acknowledge the assistance of Professor H. Morawetz and financial

(11) H. Morawetz in "Chemical Reactions of Polymers," E. M. Fettes, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp. 10-43.

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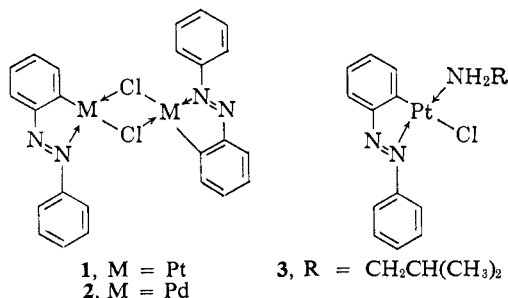
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Formation of Covalent Bonds from Platinum or Palladium to Carbon by Direct Substitution

Sir:

An unusual reaction has been found between aromatic azo compounds and potassium tetrachloroplatinate(II) or palladium(II) dichloride.

Azobenzene and potassium tetrachloroplatinate(II) were dissolved in a mixture of dioxane and water and allowed to stand at room temperature for 2 weeks. A dark maroon material was isolated by evaporating the mixture to dryness and by extracting the residue with benzene. About 48% yield of a compound believed to have structure **1** was obtained.¹ Compound **1** does not melt before decomposition, which occurs at about 270°. The palladium analog **2** melts at 279–281° dec.



The infrared spectrum (KBr pellet) of the platinum compound (**1**) reveals major absorptions at 3050, 1580, 1450, 1360, 1320, 1305, 765, 720, and 695 cm.⁻¹; ultraviolet spectrum (m μ (ϵ)): $\lambda_{\text{max}}^{\text{EtOH}}$ 257 (34,400) 350 (19,700), 373 (sh), 390 (sh), 440 (6320), and 535 (3870).

Compound **1** did not liberate azobenzene upon treatment with an excess of potassium cyanide, triphenylphosphine, or amines. Rather, new complexes were produced. For example, isobutylamine in benzene transformed compound **1** to a material assigned structure **3** (m.p. 162–164°). The ultraviolet spectrum of compound **3** and its infrared spectrum between 1300 and 1600 cm.⁻¹ are similar to those of complex **1**.

The azobenzene–platinum chloride complex (**1**) underwent decomposition upon treatment with lithium aluminum hydride in tetrahydrofuran to yield hydrazobenzene (90%).

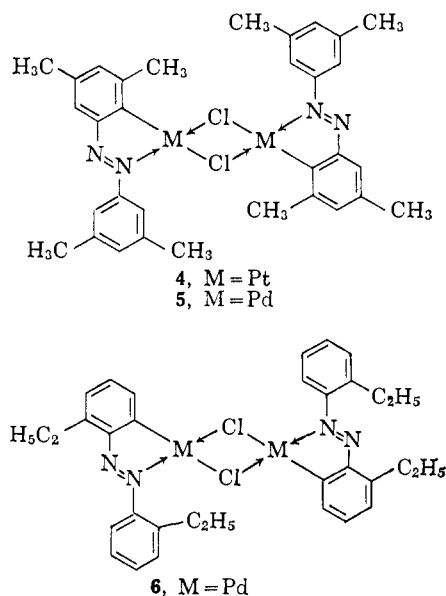
The presence of a bond between the metal atom and an *ortho* carbon atom of the azobenzene molecule was established as follows. Complex **1** was treated with lithium aluminum deuteride. After decomposition of the reaction mixture with water, the resulting hydrazobenzene was oxidized with air or mercuric oxide to azobenzene for convenience of analysis. Mass spectrometric analysis of azobenzene from two decompositions showed the following deuterium content: (A) 23% d₀, 75% d₁, 2% d₂ species; (B) 24% d₀, 74% d₁, 2%

(1) Satisfactory microanalytical data have been obtained for each of the compounds described.

d₂ species. When the reduction of compound **1** was modified by using deuterium oxide to hydrolyze the reaction mixture, the azobenzene was found to contain 4% d₀, 93% d₁, and 3% d₂ species.

Azobenzene-2-d₁, azobenzene-3-d₁, and azobenzene-4-d₁ were synthesized by standard reaction sequences.^{2,3} The nuclear magnetic resonance spectra of these deuterated azobenzenes differed slightly from each other and the spectrum of the material obtained from compound **1** was identical with the spectrum of azobenzene-2-d₁.

Compounds **4** (decomposition at 295°) and **5** (m.p. 270–275° dec.) were prepared and decomposed with lithium aluminum deuteride to yield 3,5,3',5'-tetramethylazobenzene after work-up with deuterium oxide and oxidation of the product with mercuric oxide. The platinum complex **4** afforded an azo compound in 89% yield which was found by mass spectrometry to contain 8% d₀ and 91% d₁ species. The tetramethyl-



azobenzene obtained in like manner from compound **5** contained 5% d₀ and 94% d₁ species. Both samples of tetramethylazobenzene showed nuclear magnetic resonance absorption for the protons *ortho* to the nitrogen atoms as a singlet at 7.45 p.p.m. (below tetramethylsilane), while the protons *para* to the nitrogen atoms absorbed at 7.0 p.p.m. The ratio of the areas of the absorptions was *ortho/para* = 3:2 for both samples, indicating that deuterium had been substituted in place of the metal atom in the *ortho* position of the tetramethylazobenzene.

The reaction of palladium(II) dichloride with azobenzene and its derivatives has been found to be more rapid than the reaction of platinum salts. For instance, compound **6** (m.p. 210–215°), derived from 2,2'-diethylazobenzene, was formed in 95% yield after 2 hr. at room temperature in methanol.

The structures proposed for the platinum- and palladium-azobenzene compounds are similar to the structure proposed for the product of reaction of dicyclopentadienylnickel and azobenzene,⁴ except that the authors represent coordinate bonding to nickel as

(2) T. Prosser and E. Eliel, *J. Am. Chem. Soc.*, **79**, 2544 (1957).

(3) H. Anspion, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 711.

(4) J. Kleiman and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 1544 (1963).