

are resolvable and are shown in Fig. 1. In **7** (22.2% Pd¹⁰⁵, $I = 5/2$) and **8** (33.7% Pt¹⁹⁵, $I = 1/2$) $|a| = 7.7 \pm 0.3$ and 82 ± 7 gauss, respectively. These results afford the initial observation of electron-nucleus hyperfine splittings by these nuclei and represent the first characterization of *paramagnetic* four-coordinate complexes of palladium and platinum.

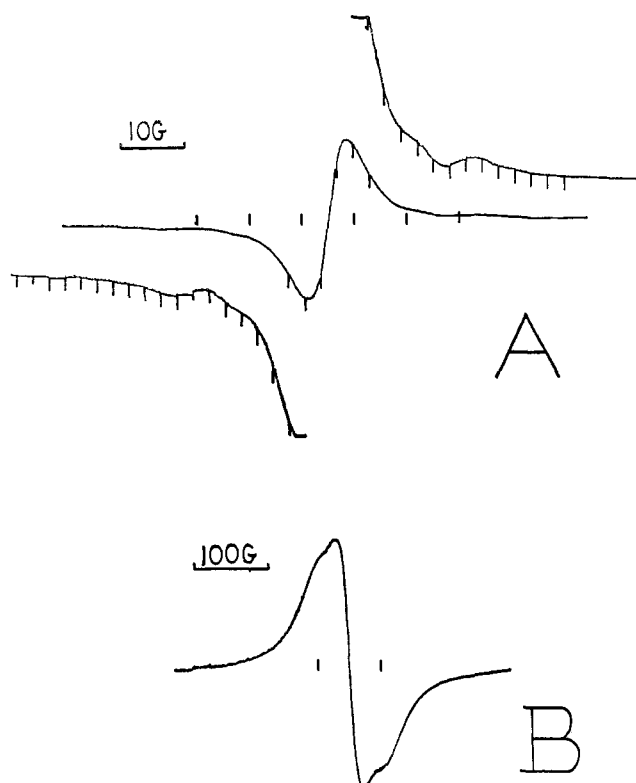


Fig. 1.—E.s.r. spectra of paramagnetic palladium and platinum complexes. A, Pd[S₄C₄(CN)₄]⁻¹ in 50% v/v. CHCl₃-dimethylformamide; offset-hyperfine splittings under higher gain; pips on signal line are 2.349 gauss apart. B, Pt[S₄C₄(CN)₄]⁻¹ in DMSO. Both solutions are $\sim 10^{-3}$ M. Centers of hyperfine components designated by short vertical lines.

Reaction of nickel carbonyl with bis-(trifluoromethyl) 1,2-dithietene,⁹ (CF₃)₂C₂S₂ (**9**) in *n*-pentane at -10° gave the dark violet crystalline complex **10** (R = CF₃, $z = 0$) in nearly quantitative yield. This compound, monomeric in solution and diamagnetic, readily abstracts electrons from basic solvents. Dissolution in dry acetone gives the anion **11** (R = CF₃, $z = -1$), which can be precipitated as the dark brown 1:1 tetraethylammonium salt. In acetone solution **11** exhibits the now characteristic e.s.r. spectrum with $\langle g \rangle = 2.0618 \pm 0.0004$. Further reduction by *p*-phenylenediamine in DMSO followed by dilution with an ethanolic solution of Et₄NBr afforded the yellow diamagnetic 2:1 salt of the anion **12** ($z = -2$).

Polarographic studies in acetonitrile solution demonstrate that **1** undergoes unusually facile reversible one-electron reduction ($E_{1/2} = +0.22$ v.) to **3** while **2**, **4** and **5** readily undergo one-electron oxidations at a platinum microelectrode ($E_{1/2} = +0.24$, $+0.46$, $+0.26$ v.¹⁰) to the corresponding anions **6**, **7** and **8**. Generation of these uni-negative species in the microwave cavity by controlled potential electrolysis¹¹ in acetonitrile solution affords e.s.r. spectra identical with

(9) C. G. Krespan, *J. Am. Chem. Soc.*, **83**, 3434 (1961).

(10) All potentials are relative to s.c.e. and were obtained in purified acetonitrile solution containing 10^{-3} M complex and 0.05 M *n*-Pr₄NClO₄.

(11) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

those obtained from the chemically synthesized compounds.

Examination of the resonance spectra of the uni-negative anions in glass media at $\sim 100^\circ$ K. shows in all cases three well separated principal *g*-values, demonstrating marked deviations of the ligand field from axial symmetry. These results are to be contrasted with those obtained from glasses of typical square planar d⁹ Cu(II) complexes in which *g*-value anisotropy in the molecular plane has not been resolved.^{12,13} In the series R = CN, $z = -1$ the following results were obtained: Ni, $g_1 = 1.996$, $g_2 = 2.043$, $g_3 = 2.140$; Pd, $g_1 = 1.956$, $g_2 = 2.046$, $g_3 = 2.065$; Pt, $g_1 = 1.825$, $g_2 = 2.067$, $g_3 = 2.221$.

Full details of synthetic studies of these complexes and others obtained from **9** and of their magnetic and spectral properties will be reported subsequently.

Acknowledgment.—Financial support by the National Institutes of Health, National Science Foundation, and the Advanced Research Projects Agency (Contract SD-88) is gratefully acknowledged.

(12) See, for example, R. Pettersson and T. Vångård, *Arkiv Kemi*, **17**, 249 (1961); D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961); H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962).

(13) In the related complex [CuS₄C₄(CN)₄]⁻¹, only two *g*-values are obtained in a methanol glass; $g_{||} = 2.0820$, $g_{\perp} = 2.0238$ (H. B. Gray, I. Bernal and E. Billig, to be published). We thank these authors for permission to quote their results in advance of publication.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

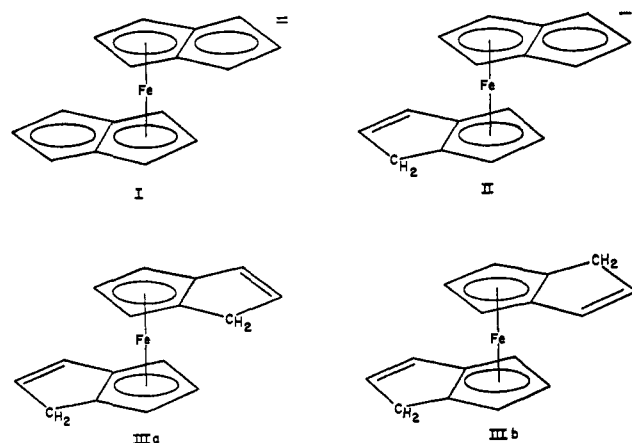
A. DAVISON
N. EDELSTEIN
R. H. HOLM
A. H. MAKI

RECEIVED APRIL 23, 1963

Ferrocene Derivatives of Pentalene: Dipentalenylyliron Dianion and Hydrodipentalenylyliron Anion

Sir:

The relationship between the pentalenyl dianion¹ and the cyclopentadienyl anion suggests that the pentalene skeleton might be incorporated into a ferrocene-like molecule. The preparation of the dipentalenylyliron dianion (I) and the hydrodipentalenylyliron anion (II) is described in this report.



Treatment of dihydropentalene in tetrahydrofuran solution with 1.1 mole equivalents of *n*-butyllithium in *n*-hexane and then with ferrous chloride furnishes in 54% yield, after aqueous work-up, sublimation (80° (3 μ)), and crystallization from *n*-hexane, red needles of dihydrodipentalenylyliron (III). [M.p. $95-99^\circ$; *Anal.* Calcd. for C₁₆H₁₄Fe: C, 73.30; H, 5.38; Fe, 21.32. Found: C, 73.38, 73.04; H, 5.68; 5.40; Fe, 21.29. $\lambda_{\text{max}}^{\text{EtOH}}$ 282 μ (ϵ 7500), 222 μ (ϵ 18700).] The bands

(1) T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).

in the nuclear magnetic resonance spectrum of III (Fig. 1) can be ascribed to the olefinic (3.92 τ ; rel. int. 3.99), ferrocenic (6.13 τ ; rel. int. 5.98) and allylic (7.33, 7.50 τ ; rel. int. 4.00) protons.²

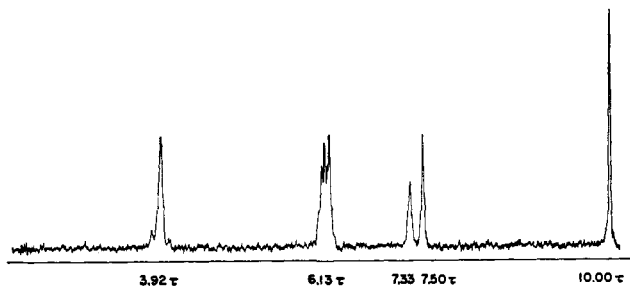


Fig. 1.—N.m.r. spectrum of III in CCl_4 determined at 60 Mc. with tetramethylsilane as an internal standard.

The ferrocene III in ether reacts with *t*-butyllithium (5 mole equivalents) in ether to yield at -40° a maroon solution, which on warming to -10° precipitates a brown solid. Addition of this suspension to excess dilute deuteriosulfuric acid and isolation of the product, as above, gives III containing two deuterium atoms (found³: 14.02, 14.42 atom % excess D, *i.e.*, 1.96, 2.02 atoms D/molecule). The n.m.r. spectrum of this material manifests the same peaks as the undeuterated compound, except that the allylic proton bands are broadened and diminished in intensity by a factor of two. (The integrated n.m.r. intensities of olefinic, ferrocenic and allylic hydrogens were found to be 3.94:6.08:2.10.)

If, however, the maroon solution formed at -40 to -50° is quenched by pouring it into 0.1 *N* deuterio-sulfuric acid (6 mole equivalents) at 0° , III is formed incorporating only one atom of deuterium (found: 7.44 atom % excess D, *i.e.*, 1.04 atoms D/molecule.⁴)

These data identify the species I and II and demonstrate their ease of formation and their stability.⁶

Acknowledgments.—We gratefully acknowledge the support of the National Science Foundation (NSF G-15561, GP-748) and the Alfred P. Sloan Foundation.

(2) The presence in the n.m.r. spectrum of two lines in the allylic region is attributed to the presence, in samples of III, of the isomers IIIa and IIIb, rather than to a chemical shift of protons *exo* and *endo* to the iron atom in one of these isomers. In the latter case, either the outer lines of the AB quartet are at least 1/10 as intense as the inner, implying that the spin-spin coupling constant is inordinately large (*ca.* 55 c.p.s.), or the outer lines overlap so closely with the inner that they cannot be resolved, implying that the coupling constant is exceptionally small (*ca.* 1 c.p.s.).

(3) Deuterium analyses by the falling drop method were performed by Josef Nemeth, Urbana, Illinois.

(4) Treatment of III with an excess of *n*-butyllithium, under a variety of conditions, and subsequent quenching of the reaction mixture with dilute D_2SO_4 , introduced only as much as 1.58 atoms of deuterium into the molecule. In other metalations *n*-butyllithium has been more effective than its branched isomers in ether, but has been less effective in petroleum ether.⁵

(5) H. Gilman and J. W. Morton, Jr., "Organic Reactions," Vol. 8, John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 284-285; H. Gilman, F. W. Moore and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

(6) Ferrocenylmethyl lithium does not appear to be preparable by metalation of methylferrocene [A. N. Nesmeyanov, E. G. Perevalova and Yu. A. Ustynuk, *Dokl. Akad. Nauk SSSR*, **133**, 1105 (1960)]. *n*-Butyllithium does, however, metalate the ferrocene nucleus to form mono- and dilithio derivatives [A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *ibid.*, **97**, 459 (1954); R. A. Benkeser, D. Goggin and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954); D. W. Mayo, P. D. Shaw and M. Rausch, *Chem. Ind. (London)*, 1388 (1957)].

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

THOMAS J. KATZ
MICHAEL ROSENBERGER

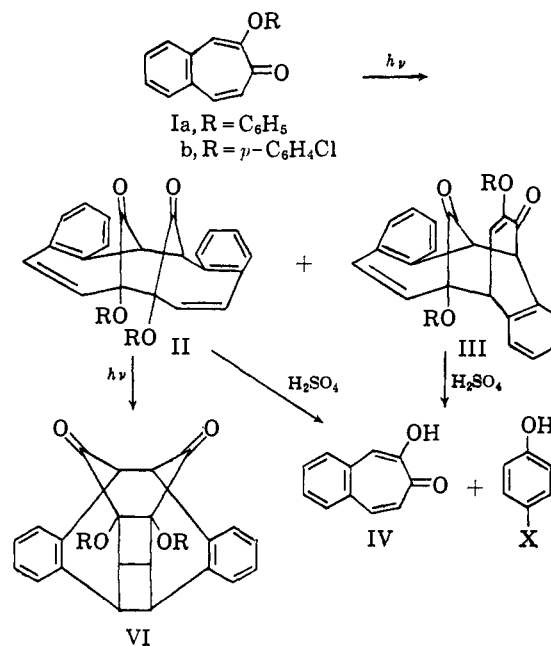
RECEIVED MAY 27, 1963

A New Photodimerization Process

Sir:

The potential photochemical rearrangements of 2-phenoxy-4,5-benzotropone (Ia) are of special interest in that the usual photochemical valence tautomerization of tropolone ethers¹ is virtually forbidden. Irradiation of Ia in 2-propanol or tetrahydrofuran (mercury arc lamp, Pyrex filter) gives IIa (27%; m.p. 208.5–210°; 217 (45,200), 255 (infl., 24,950) and 260.5 $m\mu$ (26,250); 534 (osmometric)) and IIIa (14%; 196–198°; 216 (infl., 12,600) 264 (13,200) and 273 $m\mu$ (12,600); 504 (osmometric)). Similar dimers (IIb and IIIb) may be prepared by irradiation of Ib.

Treatment of IIa,b or IIIa,b with concentrated sulfuric acid gives 4,5-benzotropone (IV) and the corresponding phenol² precluding gross rearrangement



of the carbon skeleton and suggesting that the seven-carbon ring is still intact. The infrared carbonyl absorption of IIa (5.74 μ)³ eliminates from consideration structures in which the carbonyl function is conjugated with a double bond or aromatic system. IIa shows aromatic protons (2.83 τ), an AB pattern characteristic of a styryl double bond unperturbed by protons on adjacent carbons (3.41 and 4.10 τ , $J_{ab} = 12.3$ c.p.s.) and a sharp singlet (5.64 τ). The simplicity of the n.m.r. spectrum of IIa together with the infrared and ultraviolet absorption requires a dimer composed of two units of V. A unique choice among the four possible dimers based on V is provided by the observation that irradiation of IIa (without the Pyrex filter) gives in low yield a new dimer (VI). VI shows an A_2B_2 pattern (5.61 and 6.23 τ) and a two-proton singlet (5.46 τ) in the n.m.r. spectrum and $\lambda_{\text{max}}^{\text{E}^{\text{OH}}}$ 256 (infl.; 2319), 263 (3083), 269 (3834), 273 (3300) and 306 $m\mu$ (754).

Dimer IIa is converted thermally (210°) to dimer IIIa in good yield. This unique process bears on the mechanism of the Cope rearrangement and the Diels-Alder reaction. Dimer IIIa (5.82, 5.94 μ) shows in the n.m.r. spectrum aromatic protons (2.95 τ ; eighteen

(1) O. L. Chapman, chapter in "Advances in Photochemistry," edited by W. A. Noyes, G. S. Hammond and J. N. Pitts, Interscience Publ. Co., in press.

(2) It is significant that 2-phenoxy-4,5-benzotropone is not hydrolyzed to IV under these conditions.

(3) The carbonyl absorption (in CCl_4) is lower than expected, due to strain and the effect of the adjacent phenoxy group. Cyclohexane-1,4-dione shows lower wave length infrared absorption (5.80 μ) than cyclohexanone (5.85 μ).