changes of $D_2O$ in order to re-exchange any hydrogen introduced during the isolation procedure. The protein then was thermally denaturated by allowing the sample to stand in an 80° bath for ten minutes. The denatured protein was centrifuged, washed with $D_2O$, centrifuged again, and carefully dried in vacuum. The dried protein was burned, the $D_2O$ collected and analyzed spectrophotometrically.[3] The analysis showed 98.4 atom % $D_2O$ in the water of combustion. Although this is sufficient to establish the completely deuteriated nature of the protein, an infrared examination of the material was carried out. A small amount of the protein was mixed in a mull with Perkin–Elmer fluorocarbon oil, and a search was made for the characteristic C–H absorption at 2900 to 3000 cm.$^{-1}$. No detectable C–H or N–H absorption was observed, but absorptions in the 2220 to 2240 cm.$^{-1}$ and 2450 cm.$^{-1}$ regions characteristic of C–D and N–D bonds, respectively, were present.

To establish the homogeneity and purity of the isolated protein, the visible and ultraviolet absorption spectrum, ultracentrifuge pattern, and electrophoretic properties of the deuterio- and hydrogen-protein preparations have been investigated. The absorption spectra in the visible region of both protein preparations are quite similar. In aqueous acetate buffer, pH 4.7, maximum in absorption occurs at 622 m$\mu$ in both cases, and the specific extinction coefficient (for a 0.1% solution in a 1-cm. cell) is 7.9 for the deuterio and 8.1 for the hydrogen preparation. Another maximum is observed in both preparations at 350 m$\mu$. The absorption maximum at 622 m$\mu$ indicates that the phycocyanin isolated from the deuterio and hydrogen *P. calothricoides* are definitely of the C-phycocyanin type.[4] Further absorption spectra studies showed that the ratio of optical density at 622 m$\mu$ to that in the 280 m$\mu$ region was approximately the same in both protein preparations. This indicates that the number of chromophores in both the deuterio- and hydrogen-phycocyanin molecules is very likely the same. Electrophoresis on cellulose acetate strips (acetate buffered, pH 4.70) showed a single band for both deuterio and hydrogen preparations of purified phycocyanin. The deuterio band appeared to be somewhat broader than for the hydrogen compound. Since the p*K* values for the charged groups in the two proteins are different,[5] changes in pH will affect electrophoretic behavior of the two proteins differently. The deuterio-protein definitely exhibits a lower mobility in cellulose acetate electrophoresis, and a mixture of deuterio- and hydrogen-protein is resolved into two bands on electrophoresis at pH 4.70.

The sedimentation coefficients of both protein preparations in aqueous acetate buffer (pH 4.7, $\mu$ = 0.02) were measured with Schlieren optics in the analytical ultracentrifuge. In both cases four peaks were observed. $S_{20}{}^0$ values listed for the deuterio protein are approximately 1.3 times the $S_{20}{}^0$ values for the hydrogen protein. The 14.16 *S* component in the deuterio and the 11.15 *S* in the hydrogen protein are present in the largest amount and are responsible for the major portion of the light absorption. These observations for the ordinary hydrogen-phyocyanin from *P. calothicoides* are consistent with the $S_{20}{}^0$ values originally determined by Svedberg and co-workers[6] for phycocyanin from the algae *Porphyra tenera*, *Ceramium rubrum* and *Aphanizomenon flos aquae*, and are consistent in part with the observations of Brody.[7] The pH dependence of fluorescence depolarization shown by Goedheer[8] is consistent with the kind of dissociation equilibria that probably are responsible for the observed sedimentation properties of both the hydrogen and deuterium preparations.

| $S_{20}{}^0$ for the Deuterio-phycocyanin | $S_{20}{}^0$ for the Hydrogen-phycocyanin |
|---|---|
| $4.80 \times 10^{-13}$ | $3.73 \times 10^{-13}$ |
| $8.74 \times 10^{-13}$ | $7.17 \times 10^{-13}$ |
| $14.16 \times 10^{-13}$ | $11.15 \times 10^{-13}$ |
| $22.67 \times 10^{-13}$ | $15.84 \times 10^{-13}$ |

To make meaningful comparisons possible, it is clearly essential to ascertain whether the hydrogen- and deuterio-proteins are chemically identical and differ only in isotopic composition, or whether the deuterio-protein arises from a $D_2O$ tolerant mutant organism that synthesizes phycocyanin differing in amino acid composition and sequence from the hydrogen prototype. Preliminary results obtained by Moore–Stein analysis with a Beckman Spinco amino acid analyzer indicate that the number of amino acid residues of each of the amino acids listed is identical within experimental error for both the hydrogen- and deuterio-phycocyanin: lysine, histidine, arginine, threonine, serine, glutamic acid, glycine, alanine, valine, methionine, isoleucine, leucine, tyrosine and phenylalanine. Cystine and proline are present in both the deuterio- and hydrogen-proteins, but the number of residues found differs in the two proteins by more than the experimental error. We believe that these differences result primarily from difficulties in the hydrolysis procedure, but the possibility does exist that the amino acid compositions are different. Further studies to clarify this situation are in progress.

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(4) F. T. Haxo and C. O'H Eocha, "Handbuch der Pflanzenphysiologie," Vol. V, Springer, Berlin, p. 497.

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(6) T. Svedberg and I. Erickson, *J. Am. Chem. Soc.*, **54**, 3998 (1932); T. Svedberg and T. Katsumai. *ibid.*, **50**, 525 (1928); I. G. Eriksson-Quensel, *Biochem. J.*, **32**, 585 (1938).

(7) S. S. Brody and M. Brody, *Biochim. Biophys. Acta*, **50**, 348 (1961).

(8) J. C. Goedheer, Doctoral Thesis, Rijksuniversiteit, Utrecht, 1957.

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## ADDITION OF TETRAFLUOROETHYLENE TO DICYCLOPENTADIENYLNICKEL

*Sir:*

Since the preparation of $\pi$-allylcobalt tricarbonyl,[1] several $\pi$-allyl complexes of transition metals

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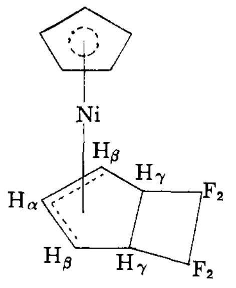
(1) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **82**, 750 (1960); see also R. F. Heck and D. S. Breslow, *ibid.*, **83**, 1097 (1961), and references cited therein.

have been characterized, *e.g.*, π-allylmanganese tetracarbonyl,[2] π-allylchloro-(triphenylphosphine)-nickel,[3] and π-allyl-π-cyclopentadienylnickel[2b] and -palladium.[2b,4] Furthermore, the allylic group can be part of a ring system as in π-cyclohexenyl-π-cyclopentadienylpalladium,[5] π-cyclopentenyl-π-cyclopentadienylnickel,[6] or the interesting nickel complex $C_{13}H_{17}NiC_5H_5$.[7] We now describe a new class of π-allylic-nickel derivatives having an unusual structure.

Dicyclopentadienylnickel (8.0 g., 42 mmoles), tetrafluoroethylene (9.3 g., 93 mmoles), dipentene (0.5 ml.),[8] and 30 ml. of tetrahydrofuran were placed in a 150-ml. steel bomb and heated (75–80°, 16 hr.). The bomb was opened, and 6.6 g. (66 mmoles) of tetrafluoroethylene was recovered. Remaining material was treated with dichloromethane and filtered. Solvents were removed (10 mm., 25°) from the filtrate. The residue was extracted with pentane and the solution chromatographed on alumina. A red band was eluted with a 4:1 pentane–benzene mixture. Removal of solvent afforded 700 mg. (5.7% yield) of moderately air stable red crystals (I),[9] m.p. 93–94° and subliming at 50° in high vacuum. *Anal.* Calcd. for $C_{12}H_{10}F_4Ni$: C, 49.9; H, 3.49; F, 26.3; Ni, 20.3; mol. wt., 289. Found: C, 49.7; H, 3.57; F, 26.1; Ni, 20.6; mol. wt. (isopiestic), 300. The structure of I was established by studying the $^1H$ and $^{19}F$ nuclear magnetic resonance spectra.[10] The proton spectrum (Table I) shows the presence of a cyclopentadienyl ring bonded to nickel,[6] as well as the presence of a π-allylic group.[3,6] The $^{19}F$ n.m.r. spectrum consists of an AB quartet.[11] This is in agreement with the structure proposed, since the presence of the nickel atom on one side of the cyclobutane ring would render the two fluorine atoms on each carbon atom non-equivalent. Chemical shifts, calculated by simple AB theory, and spin coupling constants are given in Table II. There are two possible geometric forms for I. Protons Hγ could be directed toward the nickel atom and the fluorinated cyclobutane ring could be bent away, or *vice versa*. The relative simplicity of the $^{19}F$ n.m.r. spectrum shows that one isomer predominates.



I

TABLE I

PROTON CHEMICAL SHIFTS (τ)[a]

| Compound | $H\alpha$ | $H^b$ | $H\beta$ | $H\gamma$ |
|---|---|---|---|---|
| I | 4.48[c] | 4.75 | 6.07[d] | 7.33[e] |
| II | 4.53[c] | 4.78 | 6.07[d] | 7.22[e] |

[a] Hexamethyldisiloxane as internal standard, approximately 10% solutions in trichlorofluoromethane. Relative intensities of absorptions are 1:5:2:2 for Hα, $H^b$, Hβ, and Hγ, respectively. [b] Cyclopentadienyl ring protons. [c] Triplet, $J \sim 5$ c.p.s. [d] Complex multiplet, width ~ 10 c.p.s. [e] Unresolved multiplet, width ~30 c.p.s. The halogen atoms in I and II appear to have an unshielding effect on the Hγ protons since the resonance of the corresponding protons in π-cyclopentadienyl-π-cyclopentenylnickel occurs near 8.93 τ.[6]

TABLE II

$^{19}F$ CHEMICAL SHIFTS AND SPIN COUPLING CONSTANTS[a]

| Compound | I | | II | |
|---|---|---|---|---|
| Frequency, Mc. | 40 | 56.4 | 40 | 56.4 |
| δ, p.p.m. | 116.3[b] | 116.3[b] | 107.8[b] | 107.7[b] |
| $J_{AB}$, c.p.s. | 211 | 213 | 205 | 205 |
| $\delta_{AB}$,[c] p.p.m. | 5.44 | 5.45 | 17.8 | 17.7 |
| δ′,[d] p.p.m. | ... | ... | 109.0[e] | 108.5[e] |
| $J_{AB}'$,[d] c.p.s. | ... | ... | 208 | 208 |
| $\delta_{AB}'$,[c,d] p.p.m. | ... | ... | 4.28 | 4.27 |
| $\delta_{CFCl}*$,[f] p.p.m. | ... | ... | 117.1[g] | 116.9[g] |
| $\delta_{CFCl}‡$,[f] p.p.m. | ... | ... | 126.5[h] | 126.1[h] |

[a] Studied in 10% $CCl_3F$ solutions. Chemical shifts (δ and δ′) are relative to the solvent increasing to high field, and are measured from center of AB quartets. [b] The two low-field members of this AB quartet are split further into triplets (separation of ~8 c.p.s., independent of applied field) suggesting that just one of the fluorine atoms is spin coupled to the two Hγ protons.[12] [c] $\delta_{AB}$ is chemical shift difference between A and B. [d] δ′, $J_{AB}'$ and $\delta_{AB}'$ refer to second AB system. [e] All four lines of quartet are split into triplets, with separations of two high-field members ~8 c.p.s., and with separations of two low-field members ~3 c.p.s. Splittings are independent of applied field and are presumably due to spin coupling with Hγ protons. [f] $\delta_{CFCl}*$ and $\delta_{CFCl}‡$ are the chemical shifts of the F atoms in the CFCl groups of the two isomers present. Only if the two isomers were separated could one AB quartet and CFCl resonance be assigned to one isomer and the second AB quartet and CFCl resonance to the other isomer. [g] Multiplet (~18 c.p.s. width, independent of applied field) probably due to coupling with Hγ and to a smaller extent with the $CF_2$ fluorine atoms. [h] Singlet, therefore, any coupling of CFCl signal with $CF_2$ on neighboring carbon must be small.[12]

Addition of fluoroölefins to dicyclopentadienylnickel may be quite general.[13] Thus chlorotri-

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(2) (a) H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforschg.*, **15b**, 682 (1960); (b) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

(3) R. F. Heck, J. C. W. Chien and D. S. Breslow, *Chemistry and Industry*, 986 (1961).

(4) B. L. Shaw, *Proc. Chem. Soc.*, 247 (1960).

(5) B. L. Shaw and N. Sheppard, *Chemistry and Industry*, 517 (1961).

(6) (a) M. Dubeck and A. H. Filbey, *J. Am. Chem. Soc.*, **83**, 1257 (1961); (b) E. O. Fischer and H. Werner, *Tetrahedron Letters*, No. 1, 17 (1961); (c) D. Jones, G. W. Parshall, L. Pratt and G. Wilkinson, *ibid.*, No. 2, 48 (1961).

(7) R. Criegee and P. Ludwig, *Ber.*, **94**, 2038 (1961).

(8) Polymerization inhibitor for tetrafluoroethylene.

(9) In contrast to the work described here, it has been reported recently by H. H. Hoehn, L. Pratt, K. F. Watterson and G. Wilkinson, *J. Chem. Soc.*, 2738 (1961), that dicyclopentadienylnickel and tetrafluoroethylene do not yield an isolable complex.

(10) $^1H$ spectra were obtained using a Varian A-60 spectrometer. Chemical shifts and spin coupling constants were obtained from calibrated traces. $^{19}F$ spectra were obtained by means of a Varian V4300 B high-resolution spectrometer equipped with flux stabilizer and operating at 40 and 56.4 mc. Line positions were measured using a precision audio-oscillator monitored by a frequency counter. Values reported were determined by the method of superposition, or are the averages from at least six calibrated traces.

(11) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 119.

(12) Similar behavior has been observed in a number of cyclic fluorocarbons: see W. D. Phillips, *J. Chem. Phys.*, **25**, 949 (1956).

(13) Dimethyl acetylenedicarboxylate also adds to dicyclopentadienylnickel in a 1:1 ratio. The adduct has been assigned a structure

fluoroethylene and dicyclopentadienylnickel in diglyme yield II, as red crystals of m.p. 68–73°. *Anal.* Calcd. for $C_{12}H_{10}F_3ClNi$: C, 47.2; H, 3.3; Cl, 11.6. Found: C, 47.3; H, 3.26; Cl, 11.5. The $^1$H and $^{19}$F n.m.r. spectra of II establish a structure similar to I. Proton spectra of the two complexes are nearly identical (Table I). The $^{19}$F n.m.r. spectrum of II is particularly interesting, consisting of two equally intense AB quartets and two equally intense resonances. Intensity ratio of the AB quartets to the single fluorine resonances is 2:1. Thus each AB quartet corresponds to a $CF_2$ group, and each single fluorine resonance to a fluorine atom of a CFCl group. For each of two possible arrangements of the bicyclic system in II, with the H$\gamma$ protons pointed toward and the fluorinated cyclobutane ring bent away from the nickel atom or *vice versa*, there are two alternative orientations of the CFCl group. The fluorine atom of the CFCl group may be closer to the nickel atom than the chlorine atom or the reverse may occur. Hence II could exist in four different configurations. Nevertheless, the $^{19}$F n.m.r. spectrum shows that only two forms are present. Since the two isomers are produced in equal amounts, they probably differ only in orientation of their CFCl groups.

possessing a norbornadienyl group (M. Dubeck, *J. Am. Chem. Soc.*, **82**, 6193 (1960)). We have also prepared this compound confirming the previously reported proton n.m.r. results. Neglecting those absorptions attributable to the $\pi$-cyclopentadienyl and the ester groups, there are three groups of bands with intensity ratio 2:2:1 increasing to high field. In the fluoroölefin–dicyclopentadienylnickel adducts there is also a group of three absorptions with two groups of peaks of equal intensity and one of half the intensity (Table I). However, the arrangement of these absorptions is different, being one in which there is a 1:2:2 intensity pattern increasing toward high field. Hence, in I and II the unique proton resonance appears at lowest field with chemical shift ($\tau \sim 4.5$) very different from that of the single proton ($\tau$ 7.82) in the dimethyl acetylenedicarboxylate adduct, but with chemical shift similar to that found for the corresponding central protons in other $\pi$-allylmetal complexes.[3,6] From the acetylene $CF_3C{\equiv}CCF_3$ and dicyclopentadienylnickel we have prepared a new compound having a proton n.m.r. spectrum very similar to the complex obtained by Dubeck. Again, with increasing field, the sequence of relative intensities for comparable absorptions is 2:2:1 rather than 1:2:2.

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## SPECIFIC, SENSITIVE ELECTRONIC DETECTION OF IODINE VIA CARRIER INJECTION INTO AN ANTHRACENE CRYSTAL

*Sir:*

It is well established in studies of the bulk conductivity of anthracene that charge carriers can be produced by a pulse of light at the crystal surface[1,2] and by electrode injection.[3] The recent work of Kearns, Tollin and Calvin[4] suggested that injection of carriers into an electron donor such as phthalocyanine or violanthrene could occur as well when an electron acceptor such as *o*-chloranil was deposited on its surface. The injection of carriers at such a surface should depend on the nature and extent of the charge-transfer interaction, and it therefore occurred to us that one might expect rather specific, sensitive changes in the bulk conductivity of an organic crystal exposed to various materials in the gas phase.

We examined the effect of exposure to iodine, water, sulfur dioxide, oxygen, hydrogen chloride and nitrogen dioxide on the bulk dark conductivity of anthracene. Single-crystal slices with large faces parallel or perpendicular to the cleavage plane were cut from large single crystals obtained from Harshaw Chemical Co., and conducting gold paint electrodes applied. The geometry was chosen to attempt to exclude rigorously surface conductance: a high impedance current electrode painted on one face of a crystal slice and a low impedance electrode surrounded by a guard ring on the other face. The crystal was mounted in a Teflon holder which in turn was placed in a glass cell, and guard rings painted around the walls of these mounts to assure no surface conducting path around the periphery of the cell. Measurements were performed using a Cary Vibrating Reed Electrometer Model 31–31V and a Keithley DC Power Supply Model 240. That surface conductance was not being measured was further established by (a) the fact that materials such as sulfur dioxide, hydrogen chloride, and oxygen known to increase the surface conductivity, probably *via* a change in surface mobility of carriers rather than through formation of additional carriers,[5] produced no effect in the present experiments; (b) the fact that when a Teflon plug (of the same size as the anthracene crystals) or a stilbene crystal were placed in an iodine ambient, no change in conductivity was observed.

Experiments were conducted both by introducing iodine into the evacuated cell or by flowing a carrier gas stream containing iodine over the crystal in the same type of cell provided with an outlet. Measurable changes in the conductivity of anthracene were observed at vapor pressures as low as $10^{-5}$ mm. in the static system and at concentrations as low as 0.2 part per million in the flow system. In the flow system response began within 10 seconds of exposure and reached 50% of its maximum value in 30 seconds with a further slow increase for 20–30 minutes. In the static system the maximum response occurred in less than 3 minutes.

The data presented are typical of the response observed. Perpendicular to the AB plane, the conductivity increased 1.5, 6 and 30 times at vapor pressures of iodine of $10^{-4}$, $10^{-2}$, and $10^{-1}$ mm., respectively. Parallel to the AB plane, no response was observed at vapor pressures lower than $10^{-3}$ mm., but above this pressure the change in conductivity was greater than that observed perpendicular to the AB plane, *e.g.*, 15 fold at $10^{-2}$ mm., and 175 fold at $10^{-1}$ mm.

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(1) See G. C. B. Garrett in "Semiconductors," edited by N. B. Hannay, Reinhold Publishing Corp., New York, N. Y., 1959, for a review of information on photoconductivity in anthracene.

(2) R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960).

(3) H. Kallmann and M. Pope, *J. Chem. Phys.*, **32**, 300 (1960).

(4) D. Kearns, G. Tollin and M. Calvin, *ibid.*, **32**, 1020 (1960); D. Kearns and M. Calvin, *J. Am. Chem. Soc.*, **83**, 2110 (1961).

(5) A. G. Chynoweth and W. G. Schneider, *J. Chem. Phys.*, **22**, 1021 (1954); A. G. Chynoweth, *ibid.*, **22**, 1029 (1954); W. G. Schneider and T. C. Waddington, *ibid.*, **25**, 358 (1956).