be related to the localization energies of the aromatic hydrocarbons (A). In Figure 1, localization energies ($-E^-/\beta$), which have been calculated by the SCF-MO method, are given in units of β.[6] The positions where electrons are localized in each anion are denoted by an asterisk. It is suggested from the results that hydrogen reacts with aromatic anions with stronger electron-donating abilities and appropriate localization energies, resulting in the formation of monohydro anion or hydride ion.

(6) G. Dallinga, A. A. Verrijn Stuart, P. J. Smit, and E. L. Mackor, *Z. Elektrochem.*, **61** 1019 (1957).

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Structure of $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl(py)}_2]\cdot\text{py}$, an Authenticated π Complex Containing a Three-Membered Aromatic Ring

Sir:

We wish to report the first authenticated example of a transition metal π complex with a three-membered aromatic ring system.

On the basis of infrared and magnetic data, Gowling and Kettle[1] reported that the reaction of Ni(CO)_4 with a methanolic solution of triphenylcyclopropenyl bromide gave the π-bonded complex $[(\pi\text{-Ph}_3\text{C}_3)\text{NiBr(CO)}]_2$ (I). Repeated attempts to obtain crystals of I suitable for single-crystal X-ray studies failed. However, treatment of the analogous chloride dimer, $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl(CO)}]_2$, with pyridine leads to evolution of carbon monoxide and formation of red crystals[2] of the pyridine monomer $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl(py)}_2]\cdot\text{py}$ (II). *Anal.* Calcd for $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl(C}_5\text{H}_5\text{N)}_2]\cdot\text{C}_5\text{H}_5\text{N}$: Ni, 9.81; C, 72.21; H, 5.05; N, 7.02; Cl, 5.92. Found: Ni, 10.24; C, 71.40; H, 4.80; N, 7.35; Cl, 6.24. The infrared spectrum of II (KBr pellet) shows peaks at 1370 and 1350 cm^{-1} which can be assigned to the cyclopropenyl vibrations. Faraday balance techniques show the complex to be diamagnetic.

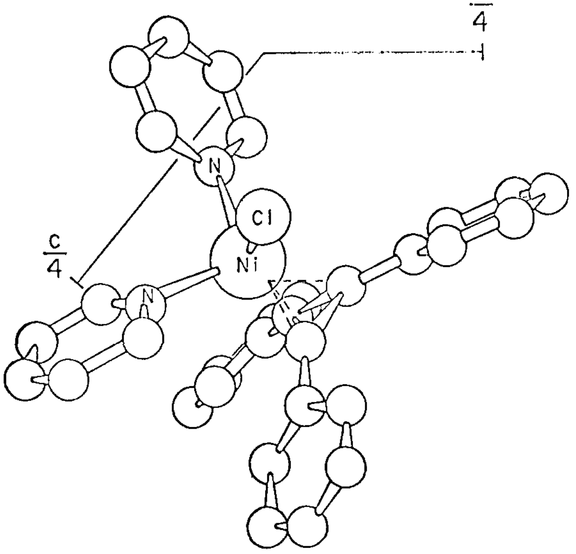

Figure 1. A molecule of $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl(py)}_2]$ viewed down the crystallographic *b* axis. The pyridine of crystallization is not shown.

Crystals of $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl(py)}_2]\cdot\text{py}$ form as maroon parallelepipeds in the monoclinic space group $P2_1/c$, $a = 16.570$ Å, $b = 10.538$ (1) Å, $c = 22.483$ (5) Å, $\beta = 129.14$ (1)°, $Z = 4$. Intensity data were collected on a G.E. XRD-5 diffractometer up to $2\theta = 100°$ with Cu Kα radiation by the "moving-crystal, moving-counter" method. The structure was solved by the usual heavy-atom techniques and refined to a conventional *R* factor of 9.7% for the 2469 independent reflections above background.

If the triphenylcyclopropenyl ring is considered to occupy one coordination position, the geometry around the central nickel atom is a distorted tetrahedron as can be seen in Figure 1. The angles around the central metal atom range from 96.0 (4) to 125.7 (4)° with an average value of 108.5° when nickel is regarded to be formally bonded to the center of the cyclopropenyl ring. The nickel–carbon (ring) distances are 1.896 (9), 1.948 (9), and 1.977 (9) Å and are considered to be chemically equivalent. These distances can be compared with those found in other nickel π-bonded aromatic systems such as $[(\pi\text{-Me}_4\text{C}_4)\text{NiCl}_2\cdot{}^1/_2\text{C}_6\text{H}_6]_2$ (1.997–2.047 Å)[3] and $(\pi\text{-C}_5\text{H}_5)\text{NiC}_5\text{H}_5\text{C}_2(\text{COOCH}_3)_2$ (2.091–2.191 Å).[4] A comparison of nickel–ring distances for the above three complexes shows them to be independent of the size of the aromatic ring: this complex, 1.76 (1) Å; the complex containing a four-membered ring, 1.749 (9) Å; and the π-cyclopentadiene complex, 1.75 (1) Å. Other pertinent distances include the two Ni–N distances of 2.043 (8) and 2.019 (7) Å and a Ni–Cl distance of 2.322 (3) Å.

Comparison of the free and complexed ligand shows similar trends to those noted for other π-aromatic complexes.[5] The three carbon–carbon distances of the cyclopropenyl ring are all equal within experimental error to an average value of 1.422 (8) Å. This is somewhat longer than the value of 1.373 (5) Å found for the free ligand[6] in $(\text{Ph}_3\text{C}_3)(\text{ClO}_4)$. An increase of this magnitude is also found when free benzene distances (1.392 Å) are compared to the average carbon–carbon distances (1.419 Å) found[5] for five π-aromatic complexes of benzene. An average exocyclic C–C distance of 1.463 (11) Å and an angle of 145.1 (4)° were determined for the nickel compound, while the values found[6] in $(\text{Ph}_3\text{C}_3)(\text{ClO}_4)$ were 1.436 (5) Å and 150.0 (3)°, respectively.

The complexed ligand can be loosely described as a shallow saucer with intra- and intermolecular steric crowding forcing the phenyl groups to twist and bend out of the plane of the cyclopropenyl ring. Deviations from planarity of this type are also evident for the phenyl groups in the complex[7] $(\pi\text{-Ph}_4\text{C}_4)\text{Fe(CO)}_3$.

(1) E. W. Gowling and S. F. A. Kettle, *Inorg. Chem.*, **4**, 604 (1965).
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(3) J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962).
(4) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 713 (1963).
(5) P. J. Wheatley, *Perspectives Struct. Chem.*, **1**, 1 (1967).
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The nickel–cyclopropenyl ring bonding can probably best be described using an MO model similar to that initially invoked[8] for symmetrically bonded cyclobutadiene complexes. Assuming C_{3v} localized symmetry, the a_1 and e combinations of the three $p\pi$ atomic orbitals of the cyclopropenyl ring interact with the nickel atomic orbitals to give bonding and antibonding molecular orbitals. An electron pair, which is formally donated from the cyclopropenyl ring to the nickel atom, resides in the a_1 bonding nickel–cyclopropenyl ring orbital, and the antibonding e orbital combination provides a pathway for electron density drift back to the cyclopropenyl ring. Using this formalism, the complex attains the inert gas configuration. An interesting result of this work is an internally consistent experimental determination of 1.33 Å for the tetrahedral Ni(0) covalent radius. This is based upon the Ni–N and Ni–Cl bond lengths which would not be affected by appreciable multiple bond character.

Acknowledgments. We wish to thank E. W. Gowling for a generous supply of triphenylcyclopropenyl chloride. We gratefully acknowledge the National Science Foundation for financial support of this research.

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Optical Detection of Transient Solvated Electrons in Pulse-Irradiated Viscous Squalane[1]

Sir:

Considerable physical and chemical evidence exists for the formation of ionic species in irradiated hydrocarbon glasses and liquids.[2] Optical and electron spin resonance studies[3] show that electrons can be stabilized in glasses at −196° with *G* values near unity. Chemical scavenging experiments[4] on liquids indicate that ion pairs are produced with yields approaching 4 per 100 eV, most of which recombine geminately, but some become uniformly distributed before reacting. Conductivity measurements[5] on these liquids provide direct evidence for such separated free ions. In the interest of linking together the glass and liquid results, viscous squalane ($C_{30}H_{62}$, mp $\sim -80°$, $\eta_{-80°} \sim 10^6$ P) was pulse irradiated in an intermediate temperature–viscosity region and optically monitored in the near-infrared. This preliminary report deals briefly with the main observations and consequent implications for the nature of electrons in hydrocarbons and the mechanism of their neutralization.

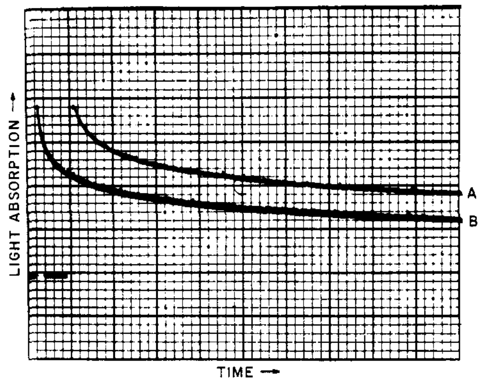

Figure 1. Decay of the solvated electron absorption at 1.6 μ in squalane at −140°. Light absorption scale: 8%/large division; time scales: (A) 50 μsec/large division, (B) 200 μsec/large division; optical path length: 2 cm; pulse duration: 5 μsec; delay between oscilloscope and accelerator triggering: 25 μsec.

In these experiments pulses of 3-MeV electrons with currents of approximately 50 mA and with durations ranging from 0.5 to 20 μsec impinged on purified squalane in a Suprasil cell mounted in a polystyrene cryostat. The dose received by a sample for a typical 1-μsec pulse was about 2×10^{17} eV/cc, and the variation in dose from pulse to pulse was monitored with charge collection devices external to the cell. A tungsten lamp, a grating spectrometer, wide-band filters, and an InAs detector comprised the optical system.

Squalane upon pulse irradiation below −70° exhibits a near-infrared absorption corresponding to a nontrivial yield of a species that decays with complex kinetics in times longer than 10^{-6} sec.

Identification of this species as a "solvated electron," e_s^-, rests on spectral and kinetic considerations.[6] The optical spectrum, determined at −130°, is very broad and appears to have a maximum in the 1.6–1.7-μ region. It is similar to trapped electron absorptions[3] found in other saturated hydrocarbons at −196°, for which confirmatory esr data exist. Moreover, in the presence of CCl_4 or C_2H_5Br, which are efficient electron scavengers, the absorption intensity and lifetime are both reduced.

The yield of e_s^- at −140° is estimated roughly as 0.6 per 100 eV by taking $\epsilon_{1.6\mu} \sim 3 \times 10^4\ M^{-1}\ \text{cm}^{-1}$.[7] With increasing temperature the dose-normalized initial optical density decreases, but this effect may be related more to electron decay during the pulse than to any inherent diminution in the yield.

The electron decay in squalane has certain features indicative of an inhomogeneous neutralization of spatially correlated ion pairs. Figure 1 shows a typical decay, the rate of which is initially very fast but becomes

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(1) Supported in part by the U. S. Atomic Energy Commission.

(2) Reviews of these subjects have appeared recently: see (a) J. E. Willard in "Fundamentals of Radiation Chemistry," P. Ausloos, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, Chapter 9; (b) R. A. Holroyd, *ibid.*, Chapter 7; (c) W. H. Hamill in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, Chapter 9.

(3) (a) J. Lin, K. Tsuji, and F. Williams, *J. Amer. Chem. Soc.*, **90**, 2766 (1968); (b) A. Ekstrom and J. E. Willard, *J. Phys. Chem.*, **72**, 4599 (1968); (c) J. B. Gallivan and W. H. Hamill, *J. Chem. Phys.*, **44**, 1279 (1966); (d) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **45**, 2723 (1967); (e) K. Tsuji, H. Yoshida, and K. Hayashi, *J. Chem. Phys.*, **46**, 810 (1967); (f) M. Shirom, R. F. Claridge, and J. E. Willard, *ibid.*, **47**, 286 (1967).

(4) For a review, see J. M. Warman, K.-D. Asmus, and R. H. Schuler in "Radiation Chemistry-II," Advances in Chemistry Series, No. 82, American Chemical Society, Washington, D. C., 1968, pp 25–57.

(5) (a) A. Hummel and A. O. Allen, *J. Chem. Phys.*, **46**, 1602 (1967); (b) P. H. Tewari and G. R. Freeman, *ibid.*, **49**, 4394 (1968); (c) W. F. Schmidt and A. O. Allen, *J. Phys. Chem.*, **72**, 3730 (1968); (d) K. Hayashi, T. Takagaki, K. Takada, K. Hayashi, and S. Okamura, *Bull. Chem. Soc. Jap.*, **41**, 1261 (1968).

(6) The term "solvated electron" as used here refers to a matrix-stabilized or localized electron, irrespective of its lifetime, in contradistinction to a quasi-free or delocalized electron (see J. Jortner in "Radiation Chemistry of Aqueous Systems," G. Stein, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, p 91).

(7) Williams and coworkers[3a] found excellent agreement in the *G* value of electrons trapped at −196° as determined by both esr measurements and optical measurements based on this value of ε determined by Gallivan and Hamill,[3c] thereby adding confidence in its use here.