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Reaction between Molecular Hydrogen and Various Electron Donor-Acceptor Complexes of Aromatic Hydrocarbons with Sodium. Their Electronic Properties¹

Sir:

It was recently reported that molecular hydrogen was dissociatively chemisorbed over some electron donor-acceptor (EDA) complexes of alkali metals with aromatic compounds such as graphite,^{2a} polycondensed hydrocarbons,^{2b} and phthalocyanides,^{2c} and the H₂-D₂ exchange reaction and hydrogenation of olefins took place markedly over these complex films at room temperature. It was also reported by Bank^{3a} and van Tamelen^{3b} that hydrogen was absorbed in the THF solution of sodium naphthalene at 25°, and sodium hydride was obtained stoichiometrically as a reaction product.

We wish to report that the activities of some aromatic mono- and dianions for the uptake of hydrogen are correlated with their electronic properties such as reduction potentials and localization energies, and the formation of the monohydro anion.

Each stoichiometric (1:1 and 1:2) EDA-complex film of aromatic hydrocarbons (*ca.* 3 × 10⁻³ mol) with sodium was deposited over a silica wool or gel from its THF solution by evacuating the solvent. Their characteristic electronic spectra show the formation of the stoichiometric EDA complexes. When hydrogen gas (10–35 cm) was admitted onto each film in the temperature range between 20 and 100°, a considerable amount of hydrogen was taken up rapidly, whereas its desorption took place very slowly under the reaction conditions. If the initial rates of uptake of hydrogen by some stoichiometric EDA-complex films at 71°, P_{H₂} = 27 cm were plotted against the reduction potentials for anion radicals and dianions of the corresponding hydrocarbons (–E', volts),^{4a} which have been measured by Hoijtink, *et al.*,^{4b} a volcano shaped curve was obtained as given in Figure 1. Hydrogen was also absorbed in the THF solution of each EDA complex in the temperature range between 20 and 60°, and the rate

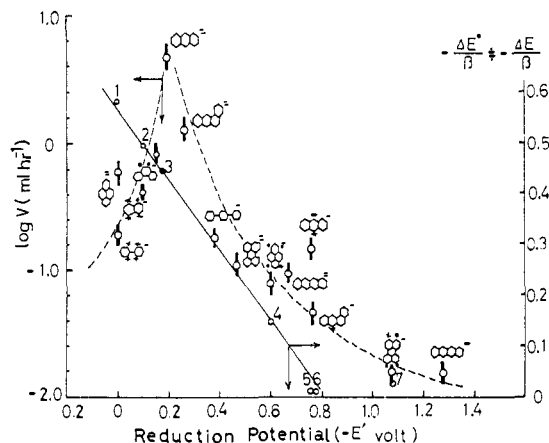


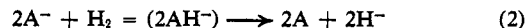
Figure 1. ---○---, the plot of the rate of hydrogen adsorption against the reduction potential for each anion radical and dianion; —○—, the plot of the localization energy of each acceptor molecule against the reduction potential for its anion radical; (1) biphenyl, (2) naphthalene, (3) phenanthrene, (4) pyrene, (5) anthracene, (6) 1,2-benzanthracene, (7) perylene.

of the uptake of hydrogen was correlated similarly with their reduction potentials as well as those over their complex films.

When hydrogen gas was introduced into each of the EDA-complex solutions of biphenyl-, naphthalene-, phenanthrene-, and anthracene- (1:1 and 1:2) sodium at 20°, it was found spectroscopically that new peaks appeared rapidly soon after the introduction of hydrogen at 425 and 500, 435, 565, and 430 mμ, respectively, which might be attributed to the formation of the corresponding monohydro anions, AH⁻Na⁺, where A denotes each of the aromatic hydrocarbons. For sodium-biphenyl, -naphthalene, and -phenanthrene complexes, the corresponding new absorption peaks decreased gradually and disappeared considerably in several hours, and a small amount of sodium hydride was detected in the reaction systems.⁵ For the complex films (deposited over a silica wool) of biphenyl-, naphthalene-, phenanthrene-, anthracene- (1:1 and 1:2), and pyrene- (1:1 and 1:2) sodium, sodium hydride was also obtained considerably in the complex films when hydrogen was sorbed in the temperatures above 60°.

Monohydro anions of anthracene (430 mμ), pyrene (455 and 525 mμ), and perylene (470 mμ) were comparatively stable in the solution at 20°, and similar absorption peaks of the corresponding monohydro anions were also observed when hydrogen was admitted onto the thin films of the EDA complex of sodium with anthracene (1:1 and 1:2), pyrene (1:1 and 1:2), and perylene (1:2) in the temperature range between 40 and 110° in several hours. On the other hand, no peaks of monohydro anions of biphenyl, naphthalene, and phenanthrene were detected in the films probably due to their instability even when hydrogen was introduced.

Hydrogen molecule seems to be activated by the EDA complexes *via* the following steps



The stabilities of those monohydro anions (AH⁻) might

(5) S. Tanaka, M. Ichikawa, S. Naito, M. Soma, T. Onishi, and K. Tamaru, *Bull. Chem. Soc. Jap.*, **41** 1278 (1968).

(1) This communication was scheduled to be published simultaneously with a communication by Bank, *et al.* (S. Bank, T. A. Lois, and M. C. Prislowski, *J. Amer. Chem. Soc.*, **91**, 5407 (1969)).

(2) (a) M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *J. Catal.*, **9**, 418 (1967); (b) *Bull. Chem. Soc. Jap.*, **40**, 1296 (1967); (c) *Trans. Faraday Soc.*, **63** 1215 (1967).

(3) (a) S. Bank and T. A. Lois, *J. Amer. Chem. Soc.*, **90**, 4505 (1968); (b) E. E. van Tamelen and R. B. Fechter, *ibid.*, **90** 6854 (1968).

(4) (a) –E' is normalized against sodium biphenyl; (b) G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland *Rec. Trav. Chim. Pays-Bas*, **75**, 485 (1956).

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 $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl}(\text{py})_2]\cdot\text{py}$, 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 Kettle¹ reported that the reaction of $\text{Ni}(\text{CO})_4$ with a

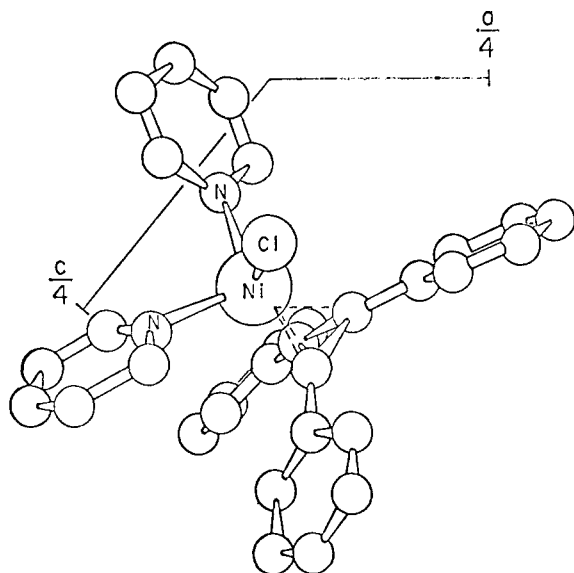


Figure 1. A molecule of $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl}(\text{py})_2]$ viewed down the crystallographic b axis. The pyridine of crystallization is not shown.

methanolic solution of triphenylcyclopropenyl bromide gave the π -bonded complex $[(\pi\text{-Ph}_3\text{C}_3)\text{NiBr}(\text{CO})_2]$ (I). Repeated attempts to obtain crystals of I suitable for single-crystal X-ray studies failed. However, treatment of the analogous chloride dimer, $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl}(\text{CO})_2]$, with pyridine leads to evolution of carbon monoxide and formation of red crystals² of the pyridine monomer $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl}(\text{py})_2]\cdot\text{py}$ (II). *Anal.* Calcd

(1) E. W. Gowling and S. F. A. Kettle, *Inorg. Chem.*, **4**, 604 (1965).

(2) This complex was first prepared by E. W. Gowling, Ph.D. Thesis, Sheffield University, 1965.

for $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl}(\text{C}_5\text{H}_5\text{N})_2]\cdot\text{C}_5\text{H}_5\text{N}$: 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.

Crystals of $[(\pi\text{-Ph}_3\text{C}_3)\text{NiCl}(\text{py})_2]\cdot\text{py}$ form as maroon parallelepipeds in the monoclinic space group $\text{P}2_1/c$, $a = 16.570 \text{ \AA}$, $b = 10.538 (1) \text{ \AA}$, $c = 22.483 (5) \text{ \AA}$, $\beta = 129.14 (1)^\circ$, $Z = 4$. Intensity data were collected on a G.E. XRD-5 diffractometer up to $2\theta = 100^\circ$ with $\text{Cu K}\alpha$ 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) $^\circ$ with an average value of 108.5 $^\circ$ 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) \AA and are considered to be chemically equivalent. These distances can be compared with those found in other nickel π -bonded aromatic systems such as $[(\pi\text{-Me}_4\text{C}_4)\text{NiCl}_2\cdot\frac{1}{2}\text{C}_6\text{H}_6]_2$ (1.997–2.047 \AA)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 \AA).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) \AA ; the complex containing a four-membered ring, 1.749 (9) \AA ; and the π -cyclopentadiene complex, 1.75 (1) \AA . Other pertinent distances include the two Ni-N distances of 2.043 (8) and 2.019 (7) \AA and a Ni-Cl distance of 2.322 (3) \AA .

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) \AA . This is somewhat longer than the value of 1.373 (5) \AA found for the free ligand⁶ in $(\text{Ph}_3\text{C}_3)(\text{ClO}_4)$. An increase of this magnitude is also found when free benzene distances (1.392 \AA) are compared to the average carbon-carbon distances (1.419 \AA) found⁵ for five π -aromatic complexes of benzene. An average exocyclic C-C distance of 1.463 (11) \AA and an angle of 145.1 (4) $^\circ$ were determined for the nickel compound, while the values found⁶ in $(\text{Ph}_3\text{C}_3)(\text{ClO}_4)$ were 1.436 (5) \AA and 150.0 (3) $^\circ$, 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 complex⁷ $(\pi\text{-Ph}_4\text{C}_4)\text{Fe}(\text{CO})_3$.

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(6) M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).

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