

show that the tetratomic ions have appearance potentials in the range 7.2–8.3 eV, and the diatomic ions have values 7.5–8.7 eV, all of which are comparable with the known ionization potentials of Bi (7.3 eV) and Sb (8.6 eV). In contrast, the triatomic ions have potentials of about 10.5 eV and have at least two possible parents of comparable or much larger intensity.

In summary, stable diatomic and tetratomic molecules exist for all possible combinations of Bi, Sb, and As. These are rather interesting from a theoretical standpoint because they form a complete class of molecules having similar bond types with systematically varying bond energies. The measurements of their dissociation energies should be of considerable value to bonding theories. These measurements and those of other thermodynamic reactions of interest, however, are enormously complicated by the incongruity of the condensed phase and the contributions of both parent and fragment species to measured ion currents.¹ It will be necessary to deal with these measurements elsewhere in more detail.

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Aromatic-Type Substitution Reactions of an Organocobalt Compound

Sir:

Although the concept of aromatic character is not well defined, organotransition metal complexes such as ferrocene and related metallocenes are generally considered aromatic in the sense that they resist ring addition and undergo various electrophilic substitution reactions. We now wish to report the first example of an organocobalt compound, π -cyclopentadienyl-tetraphenylcyclobutadienecobalt (1), which undergoes many of the ring substitution reactions that are well-documented for ferrocene.^{1,2}

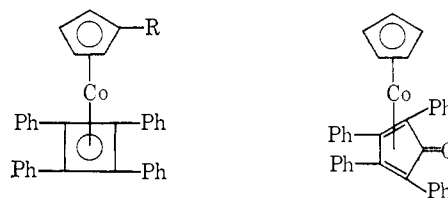
Complex 1, first described by Nakamura and Hagihara,³ has been prepared in our laboratory in ca. 60% yield by a new and improved procedure, utilizing a reaction between π -cyclopentadienylcobalt dicarbonyl and diphenylacetylene in refluxing xylene. Both 1 and the other principal product of the reaction, π -cyclopentadienyltetraphenylcyclopentadienonecobalt (2),⁴ are remarkably stable to oxidation, hydrolysis, and thermal decomposition, in contrast to most other known organocobalt compounds.

(1) (a) M. Rosenblum, "Chemistry of the Iron-Group Metallocenes," Part 1, John Wiley and Sons, Inc., New York, N. Y., 1965; (b) M. D. Rausch, *Can. J. Chem.*, **41**, 1289 (1963); (c) W. Little, *Surv. Progr. Chem.*, **1**, 133 (1963); (d) K. Plesske, *Angew. Chem. Intern. Ed. Engl.*, **1**, 312, 394 (1962).

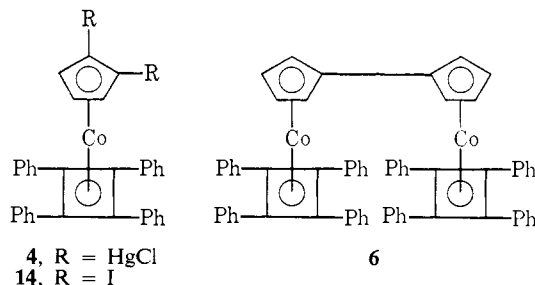
(2) Although it is claimed (J. Kozikowski, U. S. Patent 2,916,503 (Dec 8, 1959)) that the reaction of π -cyclopentadienylcobalt dicarbonyl, benzoyl chloride, and aluminum chloride produces a corresponding benzoyl derivative, no details are given.

(3) A. Nakamura and H. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961).

(4) R. Markby, H. W. Sternberg, and I. Wender, *Chem. Ind. (London)*, 1381 (1959).



- 1, R = H 9, R = COCH₃
3, R = HgCl 10, R = CHO
5, R = I 11, R = CH₂OH
7, R = CN 12, R = CH₂N(CH₃)₂
8, R = Si(CH₃)₃ 13, R = CH₂N(CH₃)₃I



Complex 1 has been found to undergo acetoxymercuration on the π -cyclopentadienyl ring, utilizing a modification of the procedure of Brown and Nelson.⁵ Following addition of lithium chloride, the chloromercuri complex 3 can be obtained in 50–60% yield, together with lesser amounts of the bischloromercuri complex 4. Iodination of 3 in methylene chloride produces the iodo complex 5 in ca. 65% yield. The latter appears to be somewhat less reactive than iodoferrocene; however, an Ullmann reaction has produced a moderate yield of the dimeric complex 6, and a Rosenmund-von Braun reaction of 5 with cuprous cyanide in N-methylpyrrolidone⁶ has afforded the cyano derivative 7 in 40–50% yield. Treatment of 3 with *n*-butyllithium produces a lithium intermediate which has been characterized in several ways, including conversion to the trimethylsilyl derivative 8 and the acetyl derivative 9.

We have also found that 1 undergoes the Vilsmeier reaction with N-methylformanilide and phosphorus oxychloride to yield, after hydrolysis, the formyl complex 10. The latter behaves as a typical aromatic aldehyde in that it undergoes the Cannizzaro reaction in ethanolic potassium hydroxide solution. One of the reaction products, the hydroxymethyl derivative 11, has also been prepared by sodium borohydride reduction of 10. Although Friedel-Crafts acetylation of 1 has thus far afforded the acetyl derivative 9 in only extremely poor yield, we have noted that 1 readily undergoes the Mannich-type aminomethylation reaction to produce a dimethylamino derivative 12 which has also been characterized as the methiodide 13.

All the new organocobalt compounds have been fully characterized by satisfactory elemental analyses and by nmr spectra, and details of their physical properties will be reported in the full paper. It is important to note, however, that the proton nmr spectra of most of the monosubstituted complexes exhibit an A₂B₂ pattern which is typical of substituted cyclopentadienyl

(5) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

(6) M. S. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961).

ring protons in many other metallocene derivatives.⁷ The structure of the dimercurated complex **4** is tentatively assigned on the basis of the nmr spectrum of its corresponding diiodo derivative **14**, which exhibits a low-field, two-proton doublet at τ 5.21, and a higher field, one-proton singlet at τ 5.49.^{8,9} The nmr spectra of the cobalt complexes are of additional interest when compared to the spectra of analogous ferrocene derivatives, since the resonances of protons on exocyclic carbon atoms (e.g., the acetyl protons of **9** at τ 8.33, the methylene protons of **11** at τ 5.91, and the trimethylsilyl protons of **8** at τ 10.2) occur at significantly higher fields than do corresponding resonances in the ferrocene series.⁷ Molecular models indicate that a substantial shielding effect may be imposed by the phenyl groups of the cyclobutadiene ring, and this effect, together possibly with metal anisotropy differences, may account for the observed chemical shifts.

The ability of **1** to undergo various electrophilic substitution reactions clearly demonstrates the aromatic reactivity of this organocobalt compound. We are currently extending the chemistry of **1** in order to compare the chemical reactivity and physical properties of this complex with other metallocene systems. Research directed toward the synthesis and reactivity of rhodium and iridium analogs of **1** is also in progress, as is the attempted formation of the parent complex, π -cyclopentadienylcyclobutadienecobalt, (π -C₅H₅)Co(C₄H₄). Reactions of the latter should prove very interesting, since Pettit and co-workers¹⁰ have already shown that cyclobutadieneiron tricarbonyl, like ferrocene, **1**, and certain other metallocenes, also undergoes ring substitution reactions of the electrophilic type.

Acknowledgment. The authors are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research.

(7) (a) M. D. Rausch and V. Mark, *J. Org. Chem.*, **28**, 3225 (1963); (b) R. A. Benkeser, Y. Nagai, and J. Hooz, *Bull. Chem. Soc. Japan*, **36**, 482 (1963); (c) G. G. Dvoryantseva, S. L. Portnova, K. I. Grandberg, S. P. Gubin, and Yu. N. Sheinker, *Dokl. Akad. Nauk SSSR*, **160**, 1075 (1965); (d) R. A. Genetti and M. D. Rausch, unpublished studies.

(8) Protons *ortho* to an iodine atom in iodobenzene and diiodobenzenes are known to be substantially deshielded with respect to other ring protons: H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); M. Martin and B. P. Dailey, *ibid.*, **37**, 2594 (1962).

(9) The structure of 1,2-dibenzoylruthenocene has been assigned on a similar basis; see ref 7a.

(10) J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3254 (1965).

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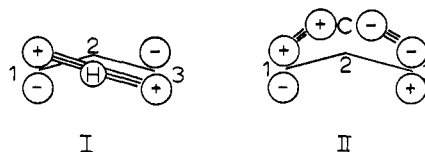
Inversion of Configuration in the Migrating Group of a Thermal 1,3-Sigmatropic Rearrangement¹

Sir:

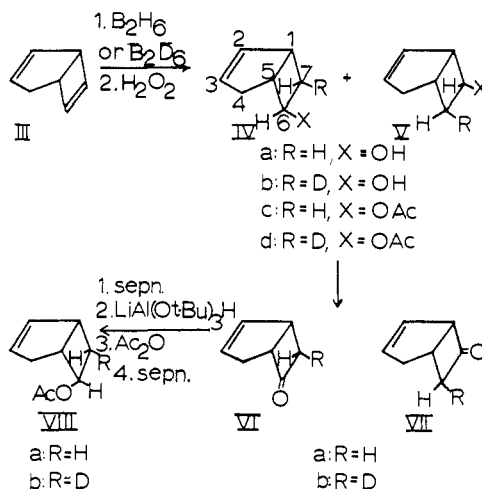
When the migrating atom in a concerted thermal 1,3-sigmatropic rearrangement is restricted to the use of a symmetric orbital to form the basis set for the transition state, bonding interactions with both ends (C-1 and C-3) of the allylic system can occur only if the process is antarafacial.² For geometric reasons, the

(1) We are indebted to the Air Force Office of Scientific Research, the Petroleum Research Fund, and the National Science Foundation for support of part of this work.

requirement is difficult to meet and, consequently, migrations of atoms in this category (e.g., hydrogen, as in I) are rare. Migrating atoms of higher atomic number (e.g., carbon, as in II), however, might use both lobes of an antisymmetric orbital and thereby achieve a suprafacial process.² This necessarily would be accompanied by inversion of configuration of the migrating group. The present paper reports the observation that, in a system constructed to force the rearrangement to be suprafacial, such an inversion does occur.



Deuterioboration-oxidation of 2,6-bicyclo[3.2.0]heptadiene (III)^{3a} gives a mixture of bicyclo[3.2.0]-2-hepten-6-*exo*-ol-7-*exo*-d (IVb) and the isomeric 7-*exo*-ol-6-*exo*-d (Vb). The corresponding acetates IVd and Vd are separable by preparative vapor chromatography (vpc).⁴ On a preparative scale, oxidation of the IVb-Vb mixture to the ketones VIb and VIIb, separation of VIb, reduction, and acetylation give bicyclo[3.2.0]-2-hepten-*endo*-6-yl acetate-*exo*-7-*d* (VIIIb) which is separated from a small amount of its *exo*-6-acetoxy isomer by vpc. Compound VIIIb has 0.94 atom of deuterium/molecule, only about 0.02 atom less enrichment than the starting IVb.



The stereochemical relationship of the deuterium and acetoxy groups in VIIIb is established as cleanly *trans* by the method of synthesis (OAc in IVd is *exo*⁵⁻⁷

(2) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(3) (a) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); (b) see also M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **83**, 3409 (1961).

(4) Identification of IVb and Vb and their acetates IVd and Vd is by vapor chromatographic retention time comparisons with those of authentic materials prepared in the undeuterated series. In the IV series authentic materials (IVa,c) were available from previous work (ref 5-7 and literature cited there). Confirmation of the structure of the V series is by conversion to bicyclo[3.2.0]-2-hepten-7-one and comparison with a sample kindly provided by Dr. D. I. Schuster.⁸

(5) J. A. Berson and J. W. Patton, *J. Am. Chem. Soc.*, **84**, 3406 (1962).

(6) J. A. Berson and R. S. Wood, *ibid.*, **89**, 1043 (1967); (b) R. S. Wood, Ph.D. Dissertation, University of Wisconsin, 1966.

(7) H. L. Goering and T. Beattie, unpublished; T. Beattie, Ph.D. Dissertation, University of Wisconsin, 1965.

(8) D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, 1911 (1963).