it is so fast as to be very close to the "high temperature limit," approximately $\sqrt{2}$.[7]

These ideas are similar to those used by Ackermann[8] to interpret the spectra of concentrated aqueous acid and base. However, the spectra are much less ambiguous, because DMSO, unlike water, does not seriously interfere with the observation of the spectrum due to the solvated proton. DMSO solutions also do not have the possibility of correlated proton motion, which may be important in the spectra of aqueous acids.

(7) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960.

(8) T. Ackermann, *Z. Physik. Chem.* (Frankfurt), 27, 253 (1961).

(9) National Science Foundation Postdoctoral Fellow, University of Minnesota, 1966–1967.

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New Gaseous Molecules of the Pnictides

Sir:

It is well known from spectroscopic and vaporization studies that the homonuclear gaseous molecules of the group Va elements (N, P, As, Sb, Bi) are diatomic and tetratomic species.[1] The dissociation energies of these molecules have been reasonably well established, and on the basis of these values one can speculate with confidence that a very large number of heteronuclear molecules formed from intercombinations of the atoms of these elements should be stable species. Until now, only a few of these possible molecules, principally the diatomic species and the tetratomic species of As–P, have been observed and studied.[2] We wish to report here experimental confirmation of the existence of additional diatomic and tetratomic molecules of these atoms.

We have investigated the gaseous molecules formed on vaporization of liquid solutions of Bi–Sb, Bi–As, and Bi–Sb–As and mixtures of the solid elements of Sb–As by mass spectrometry in the temperature range 300–750°. The samples were contained in a graphite Knudsen cell in a Bendix Time-of-Flight mass spectrometer. At the highest temperatures, the pressures of the major species were of the order of 10^{-5} atm. In general, the samples studied were not congruently vaporizing phases, so that the composition of the vapor changed slightly during an experiment. For this and other reasons, the molecules were not formed under complete equilibrium conditions.

Ions were formed by impact with 20-v electrons. Appearance potential measurements were carried out to differentiate parent and fragment ion species. Positive identification of the Sb-containing ion species was facilitated by comparing the observed relative peak intensities with those computed from the normal abundance of Sb^{121} and Sb^{123}. In all cases, however, there was no ambiguity in the assignment of the spectra because of the absence of overlapping peaks. In each of the four systems studied, all ion species were observed in *all* possible combinations of one, two, three, and four atoms, giving a total of 14 species for each of the binary systems and 34 species for the ternary system.

No ions corresponding to species containing more than four atoms were observed. Thus, the tetratomic ion species are parent ions, and consequently we may conclude that the following neutral molecules are stable species: Bi_3Sb, Bi_3As, Bi_2Sb_2, Bi_2As_2, Bi_2SbAs, $BiSb_2As$, $BiSbAs_2$, $BiSb_3$, $BiAs_3$, Sb_3As, Sb_2As_2, $SbAs_3$. In addition to these, the well-known homonuclear molecules Bi_4, Sb_4, and As_4 were observed. The appearance potentials of these molecules were comparable to the first ionization potentials of the free atoms and within their precision (±0.3 ev) varied in a reasonably systematic manner depending on the number and kind of each constituent between the limits of the atomic potentials.

The diatomic ion species were found to consist of both parent and fragment ions. The appearance potentials of the diatomic species, like those of the tetratomic ions, also had values nearly identical with the ionization potentials of the isolated atoms with similar systematic trends. Their ionization efficiency curves showed slight breaks several volts above the appearance potentials, suggesting both fragmentation contributions to the ion current and enhancement due to excitation processes. In general, the tetratomic species were in larger concentrations in the vapor, so that their electron-impact fragmentation undoubtedly contributed to the ion current enhancement at increased electron energies. On the basis of their appearance potentials, we can conclude that the following neutral diatomic molecules, in addition to the known homonuclear molecules, are stable species: BiSb, BiAs, SbAs. The first of these has been observed before in spectroscopic studies.[3]

The triatomic ions composed of all combinations of Bi, Sb, and As had appearance potentials several volts above those of the atomic, diatomic, and tetratomic ions. This is reasonable evidence that they were entirely fragments of the tetratomic molecules which were in larger concentrations. Evidence for this and other conclusions cited above are illustrated by the data given in Table I for the Bi–Sb system. The data

Table I. Relative Intensities and Appearance Potentials of Ions Observed in the Vapor from a Liquid Solution of 58 Mole % Bi and 42 Mole % Sb at 625°

Ion	Intensity	Appearance potential, ev
Sb_4^+	100	8.3
Sb^+	45	9.3[a] (IP = 8.6)
Sb_2^+	43	8.7
Sb_3^+	25	10.4[a]
$BiSb_3^+$	24	7.8
Bi^+	17	7.3[b] (IP = 7.3)
$BiSb^+$	6.7	8.0
Bi_2^+	4.2	7.5
$Bi_2Sb_2^+$	3.6	7.7
$BiSb_2^+$	2.5	10.5[a]
Bi_2Sb^+	0.4	10.6[a]
Bi_3Sb^+	0.3	7.2
Bi_4^+	0.02	7.6
Bi_3^+	~0.01	Insufficient intensity

[a] Fragment ions. [b] Standard for calibrating voltage scale.

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(1) F. J. Kohl, O. M. Uy, and K. D. Carlson, *J. Chem. Phys.*, in press.

(2) H. B. Gutbier, *Z. Naturforsch.*, **16a**, 268 (1961); K. D. Carlson, F. J. Kohl, and O. M. Uy, "Inorganic Applications of Mass Spectrometry," Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

(3) G. Herzberg, "Spectra of Diatomic Molecules," D. C. Van Nostrand Co., Princeton, N. J., 1950, p 566.

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 incongruency 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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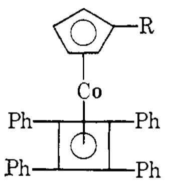
Aromatic-Type Substitution Reactions of an Organocobalt Compound

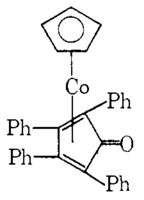
Sir:

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-cyclopentadienyltetraphenylcyclobutadienecobalt (**1**), which undergoes many of the ring substitution reactions that are well-documented for ferrocene.[1,2]

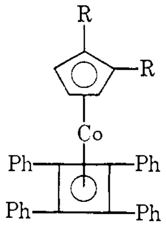
Complex **1**, first described by Nakamura and Hagihara,[3] has been prepared in our laboratory in *ca.* 60% yield by a new and improved procedure, utilizing a reaction between π-cyclopentadienylcobalt dicarbonyl and diphenylacetylene in refluxing xylene. Both **1** and the other principal product of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



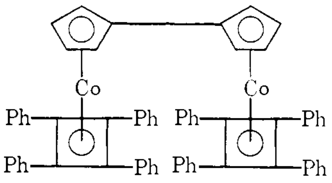
1, R = H
3, R = HgCl
5, R = I
7, R = CN
8, R = $Si(CH_3)_3$
9, R = $COCH_3$
10, R = CHO
11, R = CH_2OH
12, R = $CH_2N(CH_3)_2$
13, R = $CH_2N(CH_3)_3I$



2



4, R = HgCl
14, R = I



6

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-methylpyrrolidone[6] 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 A_2B_2 pattern which is typical of substituted cyclopentadienyl

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(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).

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(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).